*Supporting Information for*

# Cyclic (Alkyl)(Amino)Carbene Stabilized Rare Earth Metal Complexes

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# 1. X-ray Crystallography

## $^{Me}$CAAC

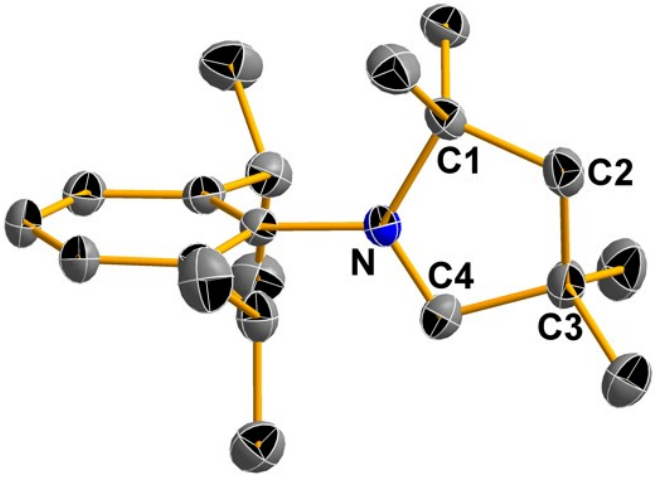



**Figure S1.** Representation of $^{Me}$CAAC with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C4 1.306(1), C4–C3 1.526(2), C3–C2 1.543(2), C2–C1 1.531(2), C1–N 1.536(1); N–C4–C3 105.66(9). Single crystals of $^{Me}$CAAC suitable for X-ray crystallography were grown from a toluene solution layered with hexanes. A total of 14042 reflections ($-11 \leq h \leq 11$, $-10 \leq k \leq 14$, $-23 \leq l \leq 21$) were collected at $T = 180$ K with $2\theta_{max} = 54.97°$, of which 4220 were unique. The residual peak and hole electron density were 0.21 and -0.19 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0284$ and GOF = 1.051. Crystal and refinement data for $^{Me}$CAAC: formula $C_{20}H_{31}N$, space group $P2_1/n$, $a = 9.1502(3)$, $b = 11.2150(4)$, $c = 18.2270(6)$, $\beta = 100.360(3)°$, $V = 1839.95(11)$ Å$^3$, $Z = 4$, $\mu = 0.058$ mm$^{-1}$, $F(000) = 632.0$, $R_1 = 0.0443$ and $wR_2 = 0.1318$ (based on all data, $I \geq 2\sigma(I)$).

**$^{Et}$CAAC**

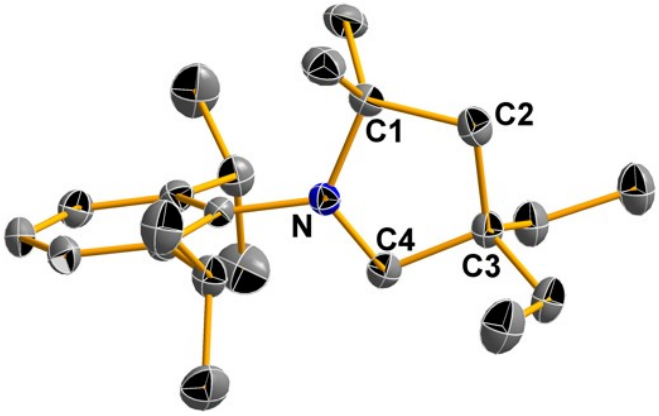



**Figure S2.** Representation of $^{Et}$CAAC with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C4 1.303(2), C4–C3 1.530(2), C3–C2 1.551(2), C2–C1 1.531(2), C1–N 1.535(2); N–C4–C3 106.3(1). Single crystals suitable for X-ray crystallography were grown from a hexanes solution. A total of 11285 reflections ($-7 \leq h \leq 9$, $-14 \leq k \leq 15$, $-15 \leq l \leq 15$) were collected at $T = 180$ K with $2\theta_{max} = 57.328°$, of which 4360 were unique. The residual peak and hole electron density were 0.23 and -0.21 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0310$ and GOF = 1.035. Crystal and refinement data for $^{Et}$CAAC: formula $C_{22}H_{35}N$, space group $P\bar{1}$, $a = 6.9854(4)$, $b = 11.7951(6)$, $c = 12.0875(6)$, $\alpha = 89.751(4)°$, $\beta = 88.772(4)°$, $\gamma = 85.990(4)°$, $V = 993.26(9)$ Å$^3$, $Z = 2$, $\mu = 0.059$ mm$^{-1}$, $F(000) = 348.0$, $R_1 = 0.0472$ and $wR_2 = 0.1236$ (based on all data, $I \geq 2\sigma(I)$).

**($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$**

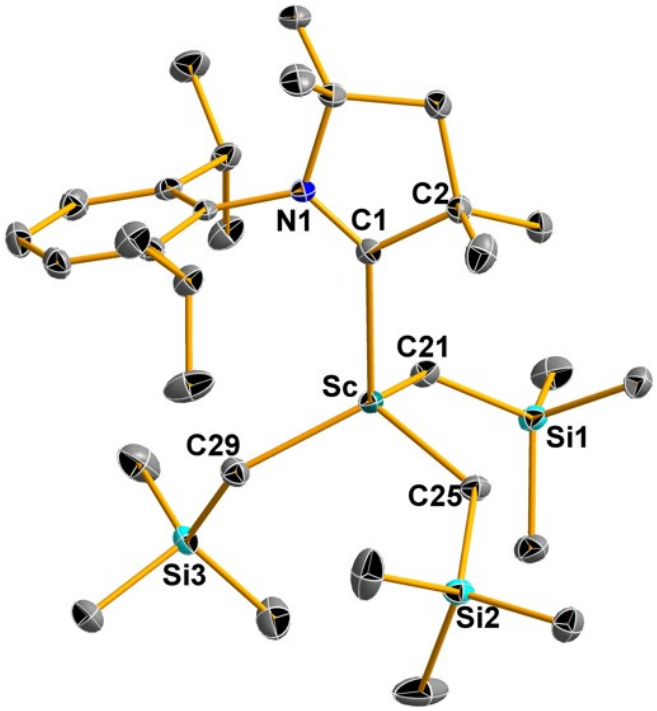



**Figure S3.** Representation of ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**1-Sc**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C1 1.305(2), C1–C2 1.525(2), Sc–C1 2.445(1), Sc–C21 2.222(1), Sc–C25 2.222(2), Sc–C29 2.213(1); C1–Sc–C21 105.14(5), C1–Sc–C25 106.98(5), C1–Sc–C29 114.54(5), C21–Sc–C25 107.48(5), C25–Sc–C29 111.11(6), C29–Sc–C21 111.15(6). Single crystals suitable for X-ray crystallography were grown from a hexanes solution. A total of 73359 reflections ($-15 \leq h \leq 29$, $-22 \leq k \leq 23$, $-56 \leq l \leq 36$) were collected at $T = 100$ K with $2\theta_{max} = 60.84°$, of which 20247 were unique. The residual peak and hole electron density were 0.77 and -0.54 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0316$ and GOF = 1.046. Crystal and refinement data for ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$: formula $C_{32}H_{64}ScNSi_3$, space group *Pbca*, $a = 21.2782(4)$, $b = 17.1989(3)$, $c = 41.7376(10)$, $V = 15274.4(5)$ Å$^3$, $Z = 16$, $\mu = 0.306$ mm$^{-1}$, $F(000) = 5216.0$, $R_1 = 0.0400$ and $wR_2 = 0.0966$ (based on all data, $I \geq 2\sigma(I)$).

**($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$**

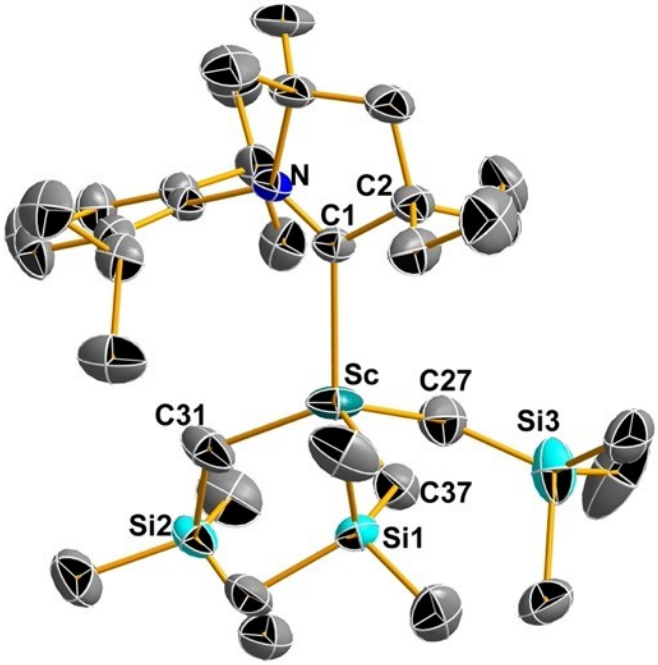



**Figure S4.** Representation of ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**2-Sc**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C1 1.296(3), C1–C2 1.526(3), Sc–C1 2.455(2), Sc–C27 2.225(3), Sc–C31 2.199(3), Sc–C37 2.261(5); C1–Sc–C27 108.1(1), C1–Sc–C31 114.2(1), C1–Sc–C37 109.0(1), C27–Sc–C31 108.2(1), C27–Sc–C37 98.1(2), C31–Sc–C37 117.7(2). Single crystals suitable for X-ray crystallography were grown from a hexanes solution. A total of 37290 reflections ($-29 \le h \le 26$, $-23 \le k \le 22$, $-26 \le l \le 32$) were collected at $T = 180$ K with $2\theta_{max} = 60.48°$, of which 10401 were unique. The residual peak and hole electron density were 1.08 and -0.97 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0471$ and GOF = 1.034. Crystal and refinement data for ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$: formula $C_{34}H_{68}NSi_3Sc$, space group *Pbca*, $a$ = 21.1966(12), $b$ = 16.7104(10), $c$ = 23.0440(14), $V$ = 8162.3(8) Å$^3$, $Z$ = 8, $\mu$ = 0.288 mm$^{-1}$, $F(000)$ = 2736.0, $R_1 = 0.0681$ and $wR_2 = 0.1662$ (based on all data, $I \ge 2\sigma(I)$).

**($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$**

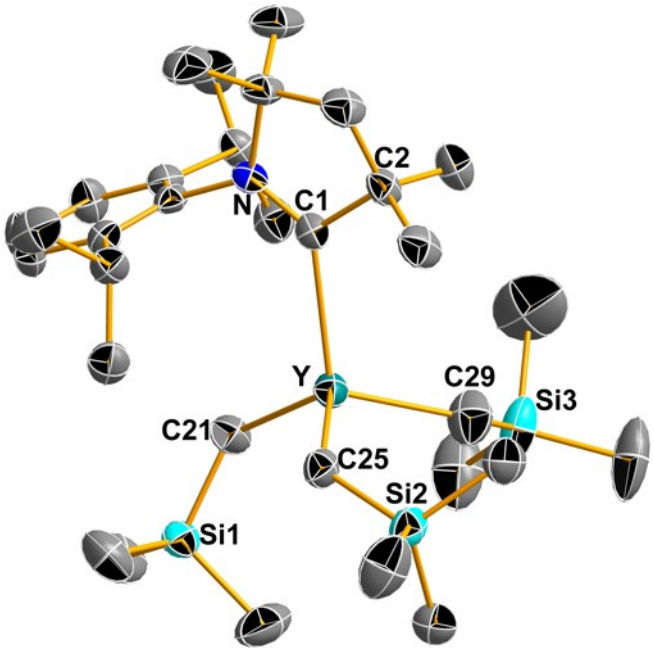



**Figure S5.** Representation of ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$ (**1-Y**) with thermal ellipsoids set at 50% probability. Hydrogen and solvent atoms were omitted for clarity. Selected distances [Å] and angles [º]: N–C1 1.297(5), C1–C2 1.516(5), Y–C1 2.579(3), Y–C21 2.363(4), Y–C25 2.381(4), Y–C29 2.354(4); C1–Y–C21 111.0(1), C1–Y–C25 107.9(1), C1–Y–C29 110.7(1), C21–Y–C25 113.1(1), C25–Y–C29 103.7(1), C29–Y–C21 110.3(1). Single crystals suitable for X-ray crystallography were grown from a hexanes solution. A total of 28254 reflections ($-10 \le h \le 13$, $-25 \le k \le 20$, $-25 \le l \le 25$) were collected at $T = 180$ K with $2\theta_{max} = 54.966°$, of which 8932 were unique. The residual peak and hole electron density were 0.76 and -0.57 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0793$ and GOF = 1.035. Crystal and refinement data for ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$: formula $C_{32}H_{64}NSi_3Y$, space group $P2_1/c$, $a = 10.0739(3)$, $b = 19.8627(9)$, $c = 19.5832(7)$, $\beta = 94.936(3)°$, $V = 3904.0(3)$ Å$^3$, $Z = 4$, $\mu = 1.604$ mm$^{-1}$, $F(000) = 1376.0$, $R_1 = 0.0680$ and $wR_2 = 0.1253$ (based on all data, $I \ge 2\sigma(I)$).

**($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$**

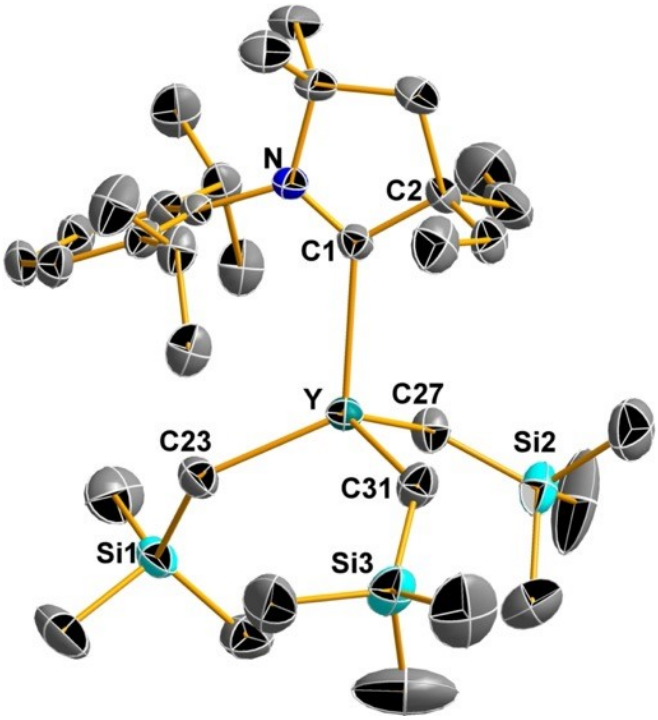



**Figure S6.** Representation of ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$ (**2-Y**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C1 1.298(3), C1–C2 1.516(3), Y–C1 2.596(2), Y–C23 2.373(3), Y–C27 2.379(3), Y–C31 2.387(3); C1–Y–C23 117.55(9), C1–Y–C27 103.12(8), C1–Y–C31 105.09(9), C23–Y–C27 111.42(9), C27–Y–C31 111.2(1), C31–Y–C23 108.2(1). Single crystals suitable for X-ray crystallography were grown from an *n*-pentane solution. A total of 26970 reflections ($-13 \le h \le 14$, $-23 \le k \le 27$, $-21 \le l \le 28$) were collected at $T = 180$ K with $2\theta_{max} = 58.96°$, of which 10852 were unique. The residual peak and hole electron density were 1.34 and -0.47 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0259$ and GOF = 1.071. Crystal and refinement data for ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$: formula $C_{34}H_{68}NSi_3Y$, space group $P2_1/c$, $a$ = 10.4317(3), $b$ = 19.7613(7), $c$ = 21.4276(8), $\beta$ = 97.418(3)°, $V$ = 4380.2(3) Å$^3$, $Z$ = 4, $\mu$ = 1.432 mm$^{-1}$, $F(000)$ = 1440.0, $R_1 = 0.0433$ and $wR_2 = 0.1147$ (based on all data, $I \ge 2\sigma(I)$).

**($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$**

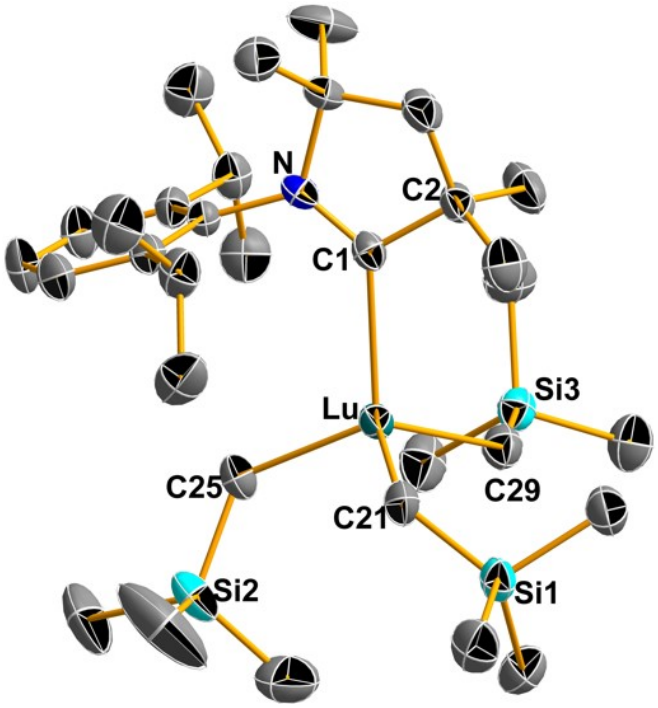



**Figure S7.** Representation of ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**1-Lu**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C1 1.302(4), C1–C2 1.525(4), Lu–C1 2.530(3), Lu–C21 2.332(3), Lu–C25 2.323(3), Lu–C29 2.340(3); C1–Y–C21 105.7(1), C1–Lu–C25 113.6(1), C1–Lu–C29 110.1(1), C21–Lu–C25 107.6(1), C25–Lu–C29 110.5(1), C21–Lu–C29 109.1(1). Single crystals suitable for X-ray crystallography were grown from a hexanes solution. A total of 92091 reflections ($-27 \leq h \leq 24$, $-21 \leq k \leq 22$, $-40 \leq l \leq 54$) were collected at $T = 180$ K with $2\theta_{max} = 54.97°$, of which 17946 were unique. The residual peak and hole electron density were 0.540 and -1.05 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0492$ and GOF = 1.012. Crystal and refinement data for ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$: formula $C_{32}H_{64}LuNSi_3$, space group *Pbca*, $a$ = 21.5528(4), $b$ = 17.1763(3), $c$ = 42.2580(6), $V$ = 15643.8(5) Å$^3$, $Z$ = 16, $\mu$ = 2.634 mm$^{-1}$, $F(000)$ = 6016.0, $R_1 = 0.0324$ and $wR_2 = 0.0654$ (based on all data, $I \geq 2\sigma(I)$).

**($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$**

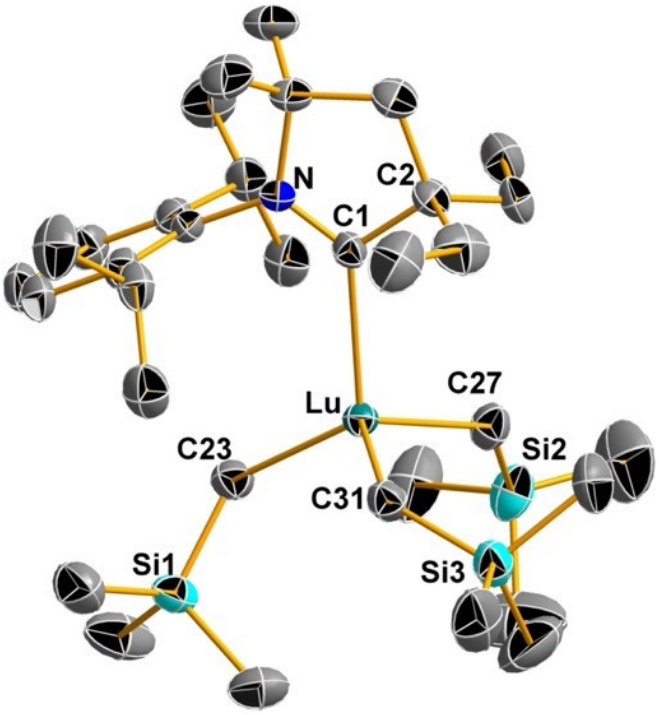



**Figure S8.** Representation of ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**2-Lu**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: N–C1 1.296(3), C1–C2 1.521(3), Lu–C1 2.539(2), Lu–C23 2.321(3), Lu–C27 2.326(2), Lu–C31 2.317(3); C1–Lu–C23 116.86(9), C1–Lu–C27 105.60(8), C1–Lu–C31 103.89(8), C23–Lu–C27 108.2(1), C27–Lu–C31 111.22(9), C31–Lu–C23 111.0(1). Single crystals suitable for X-ray crystallography were grown from an *n*-pentane solution. A total of 33192 reflections ($-8 \le h \le 14$, $-25 \le k \le 26$, $-27 \le l \le 28$) were collected at $T = 180$ K with $2\theta_{max} = 58.896°$, of which 10941 were unique. The residual peak and hole electron density were 0.45 and -0.48 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1 = 0.0246$ and GOF = 1.063. Crystal and refinement data for ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$: formula $C_{34}H_{68}NSi_3Lu$, space group $P2_1/c$, $a$ = 10.4110(2), $b$ = 19.6904(4), $c$ = 21.3623(5), $\beta$ = 97.549(2)°, $V$ = 4341.25(16) Å$^3$, $Z$ = 4, $\mu$ = 2.376 mm$^{-1}$, $F(000)$ = 1568.0, $R_1$ = 0.0265 and $wR_2$ = 0.0695 (based on all data, $I \ge 2\sigma(I)$).

**($^{Me}$CAAC)$_2$YI$_3$**

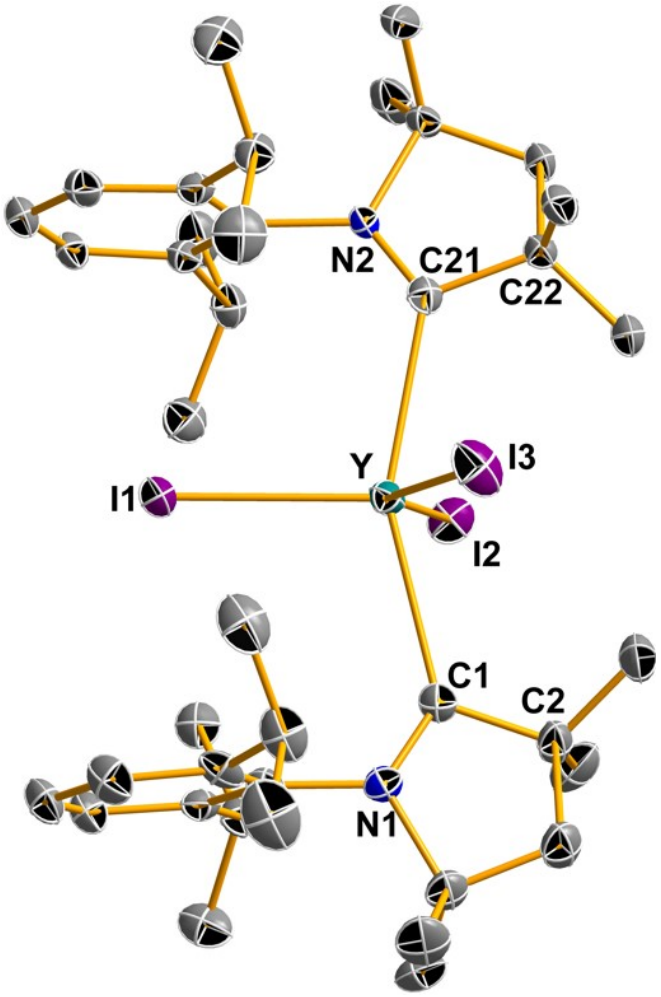



**Figure S9.** Representation of ($^{Me}$CAAC)$_2$YI$_3$ (**3-Y**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: Y–C1 2.639(4), Y–C21 2.623(4), C1–N1 1.309(5), C21–N2 1.312(5), Y–I1 2.8583(5), Y–I2 2.9614(5), Y–I3 2.9359(5), I1–Y–I2 111.69(2), I2–Y–I3 141.98(2), I1–Y–I3 106.27(2). Single crystals suitable for X-ray crystallography were grown from a toluene solution layered with hexanes. A total of 61388 reflections ($-24 \leq h \leq 24$, $-19 \leq k \leq 18$, $-28 \leq l \leq 26$) were collected at $T$ = 180 K with $2\theta_{max}$ = 61.528°, of which 13316 were unique. The residual peak and hole electron density were 0.92 and -0.64 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1$ = 0.0480 and GOF = 1.044. Crystal and refinement data for ($^{Me}$CAAC)$_2$YI$_3$ plus one $C_7H_8$ molecule: formula $C_{47}H_{70}I_3N_2Y$, space group $Pca2_1$, $a$ = 18.3616(4), $b$ = 13.3428(3), $c$ = 19.9386(5), $V$ = 4884.9(2) Å$^3$, $Z$ = 4, $\mu$ = 3.121 mm$^{-1}$, $F(000)$ = 2256.0, $R_1$ = 0.0305 and $wR_2$ = 0.0578 (based on all data, $I \geq 2\sigma(I)$).

**($^{Me}$CAAC)$_2$YbI$_3$**

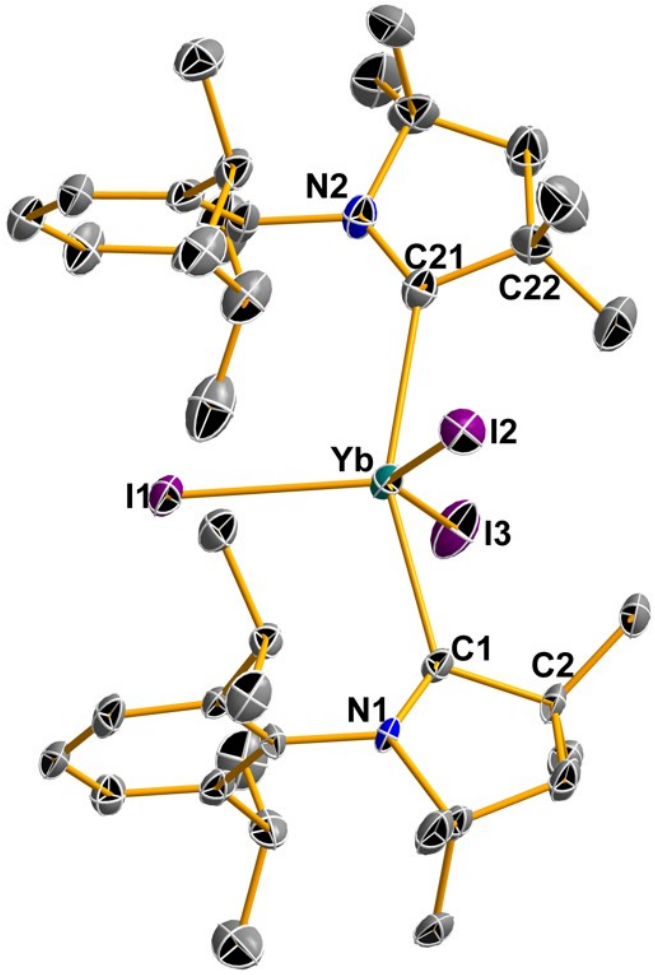



**Figure S10.** Representation of ($^{Me}$CAAC)$_2$YbI$_3$ (**3-Yb**) with thermal ellipsoids drawn at 50% probability. Hydrogen atoms and solvent molecules were omitted for clarity. Selected distances [Å] and angles [°]: Yb–C1 2.57(1), Yb–C21 2.58(1), C1–N1 1.30(2), C21–N2 1.31(2), Yb–I1 2.826(1), Yb–I2 2.918(1), Yb–I3 2.897(1), I1–Yb–I2 110.87(3), I2–Yb–I3 143.15(3), I1–Yb–I3 105.95(3). Single crystals suitable for X-ray crystallography were grown from a toluene solution layered with hexanes. A total of 40645 reflections ($-24 \leq h \leq 24$, $-17 \leq k \leq 17$, $-26 \leq l \leq 26$) were collected at $T$ = 180 K with $2\theta_{max}$ = 56.562°, of which 11597 were unique. The residual peak and hole electron density were 1.52 and -1.51 eA$^{-3}$. The least-squares refinement converged normally with residuals of $R_1$ = 0.0691 and GOF = 1.052. Crystal and refinement data for ($^{Me}$CAAC)$_2$YbI$_3$ plus one $C_7H_8$ molecule: formula $C_{47}H_{70}I_3N_2Yb$, space group $Pca2_1$, $a$ = 18.3367(5), $b$ = 13.3310(6), $c$ = 19.8826(8), $V$ = 4860.2(3) Å$^3$, $Z$ = 4, $\mu$ = 3.861 mm$^{-1}$, $F$(000) = 2380.0, $R_1$ = 0.0546 and $wR_2$ = 0.1275 (based on all data, $I \geq 2\sigma(I)$).

## 2. $^{1}$H and $^{13}$C NMR Spectra

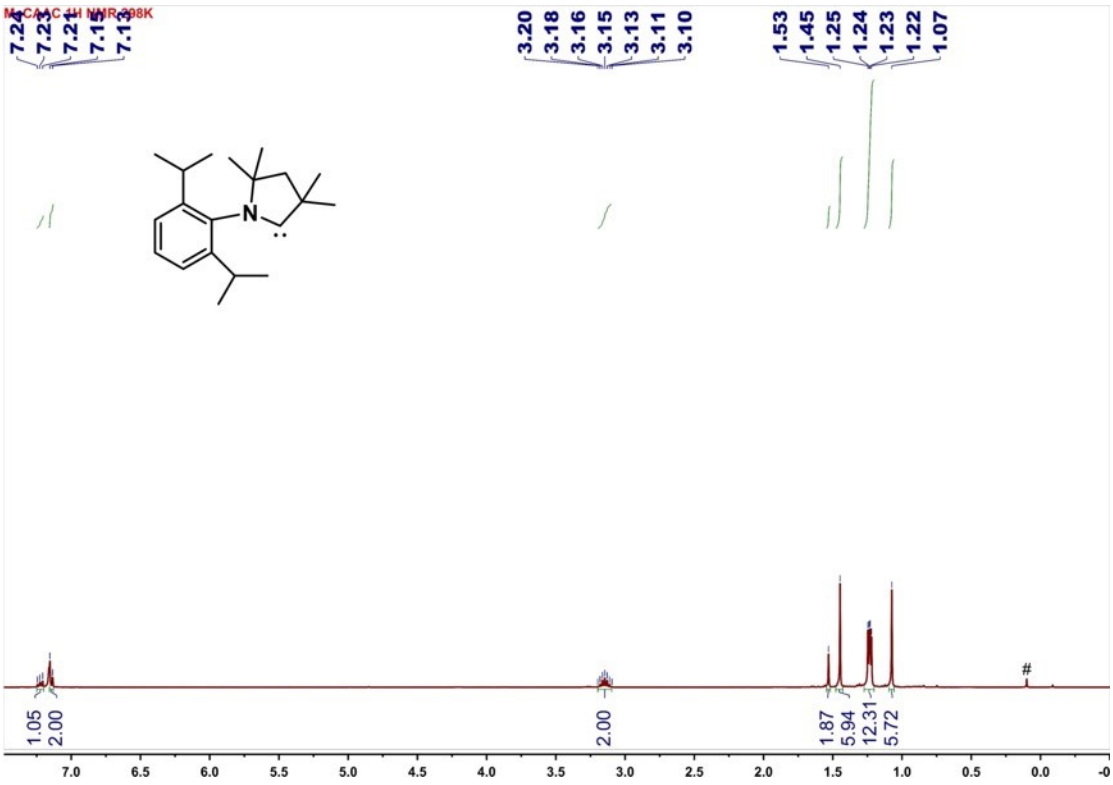



**Figure S11**. $^{1}$H NMR ($C_6D_6$, 400 MHz, 298 K) spectrum of $^{Me}$CAAC δ, ppm: 7.25–7.20 (m, 1H, *p*-C*H* of aryl), 7.14 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, *m*-C*H* of aryl), 3.15 (m, 2H, C*H*($CH_3$)$_2$), 1.53 (s, 2H, C$H_2$), 1.45 (s, 6H, NC(C$H_3$)$_2$), 1.23 (m, 12H, CH(C$H_3$)$_2$), 1.07 (s, 6H, $C_{carbene}$C(C$H_3$)$_2$). #: the methyl peak of bis(trimethylsilyl)amine, which is a by-product in this reaction and could not be fully removed by drying under reduced pressure. 1H NMR data from literature[1]: $^{1}$H NMR ($C_6D_6$, 300 MHz, 298 K) spectrum of $^{Me}$CAAC δ, ppm: 7.18 (1H), 7.11 (d, 2H), 3.11 (m, 2H), 1.50 (s, 2H), 1.41 (s, 6H), 1.20 (12H), 1.04 (s, 6H).

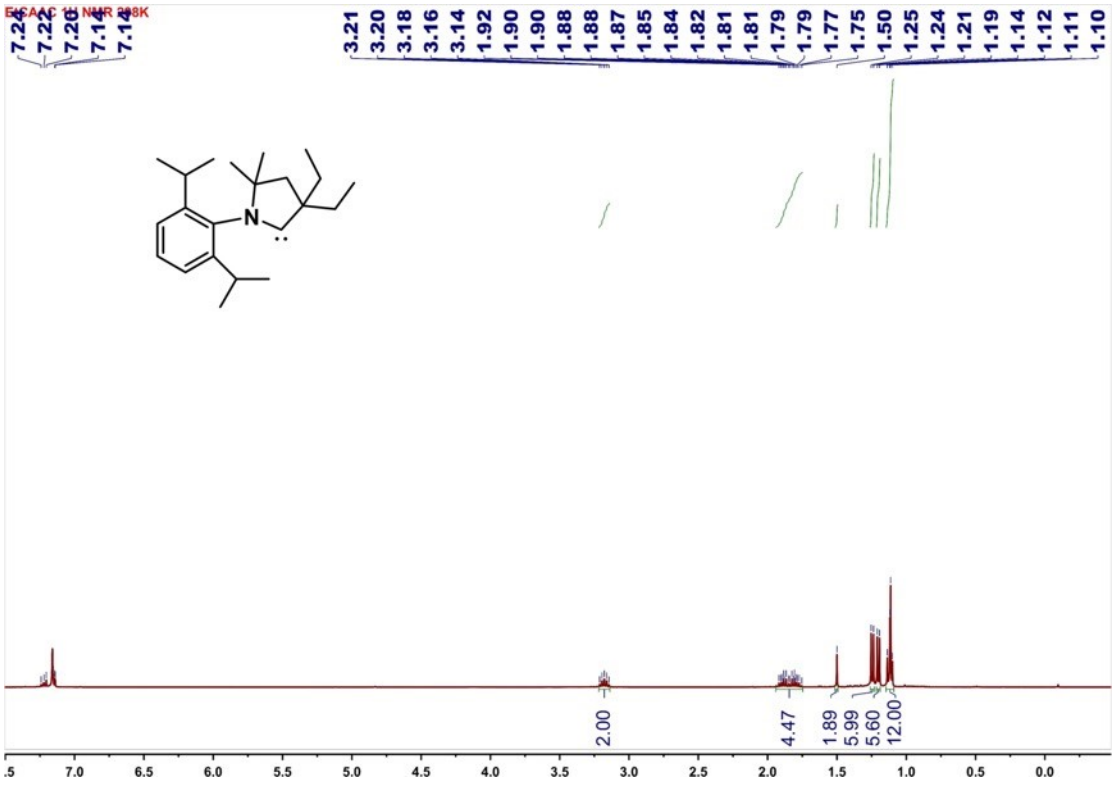



**Figure S12**. $^{1}$H NMR ($C_6D_6$, 400 MHz, 298 K) spectrum of $^{Et}$CAAC δ, ppm: 7.22–7.14 (m, 3H, C*H* of aryl), 3.18 (hept, $^{3}J_{HH}$ = 6.8 Hz, 2H, C*H*$(CH_3)_2$), 1.95-1.75 (m, 4H, C(C*H*$_2$CH$_3$)$_2$), 1.50 (s, 2H, C*H*$_2$), 1.24, 1.20 and 1.15-1.08 (18H, CH(C*H*$_3$)$_2$ and C(CH$_2$C*H*$_3$)$_2$). 1H NMR data from literature[2]: $^{1}$H NMR ($C_6D_6$, 300 MHz) spectrum of $^{Et}$CAAC δ, ppm: 7.22 (t, *J* = 6 Hz, 1H), 7.14 (d, *J* = 6 Hz, 2H), 3.16 (hept, *J* = 6 Hz, 2H), 1.83 (m, 4H), 1.50 (s, 2H), 1.24 (d, *J* = 9 Hz, 6H), 1.18 (d, *J* = 6 Hz, 6H), 1.11 (s, 6H), 1.11 (t, *J* = 6 Hz, 6H).

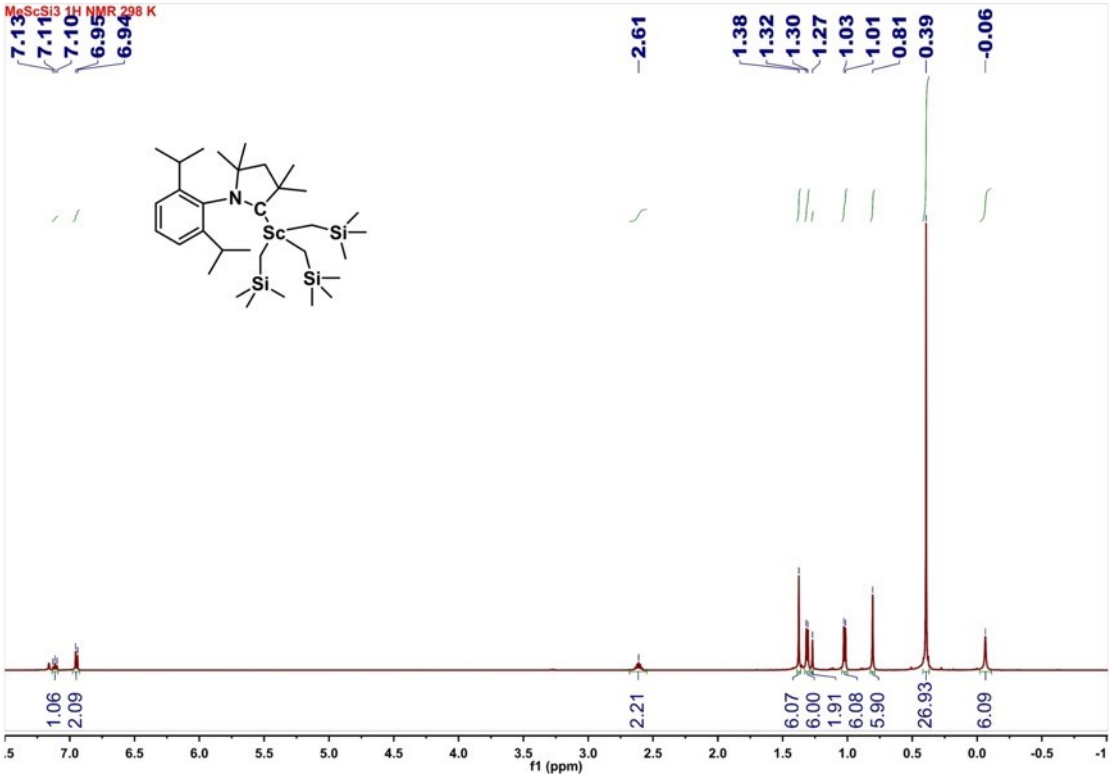



**Figure S13**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**1-Sc**) δ, ppm: 7.13 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C*H* of aryl), 6.95 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-C*H* of aryl), 2.61 (m, 2H, C*H*($CH_3$)$_2$), 1.38 and 0.81 (s, 12 H, NC($CH_3$)$_2$ and $C_{carbene}$C($CH_3$)$_2$), 1.32 and 1.03 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, CH($CH_3$)$_2$), 1.27 (s, 2H, C$CH_2$), 0.39 (s, 27H, Si($CH_3$)$_3$) and -0.06 (s, 6H, $CH_2$Si($CH_3$)$_3$).

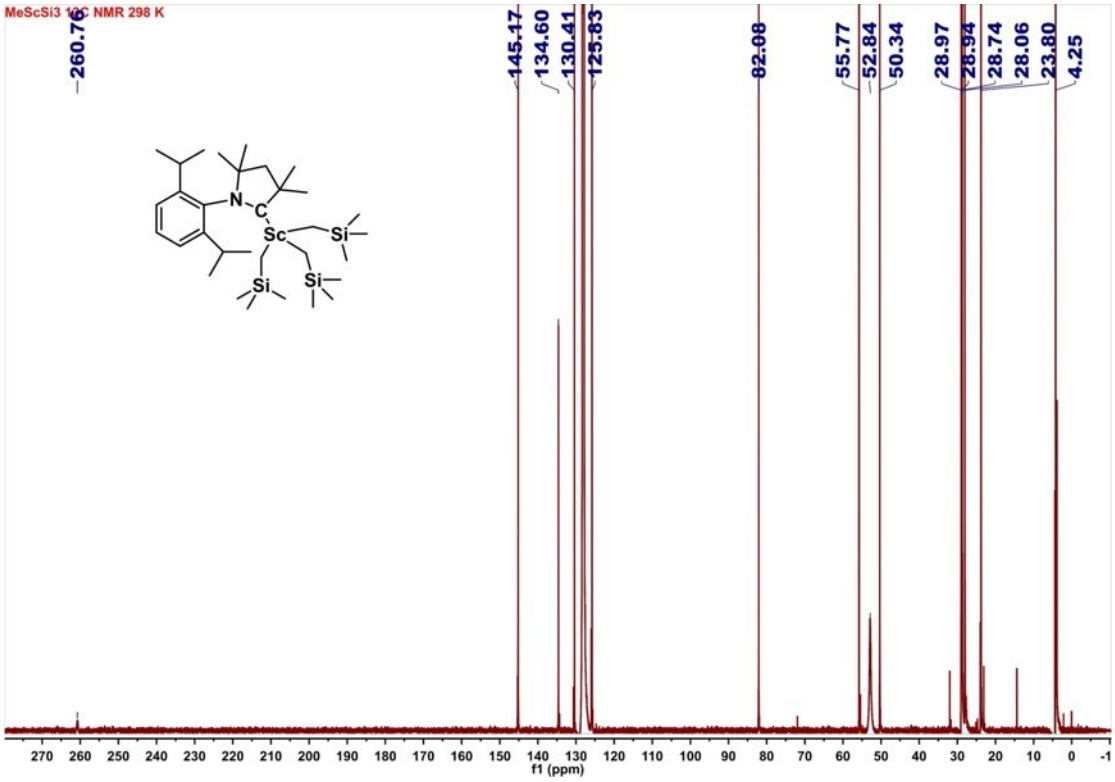



**Figure S14**. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**1-Sc**) δ, ppm: 260.76 ($C_{carbene}$), 145.17, 134.60, 130.41, 125.83 (*C*H of aryl), 82.08 (N*C*($CH_3$)$_2$), 55.77 (C*C*$H_2$), 52.84 (*C*$H_2$Si($CH_3$)$_3$), 50.34 ($C_{carbene}$*C*($CH_3$)$_2$), 28.97, 28.94, 28.74, 28.06 (*C*$H_3$), 23.80 (*C*H($CH_3$)$_2$), 4.25 (Si(*C*$H_3$)$_3$).

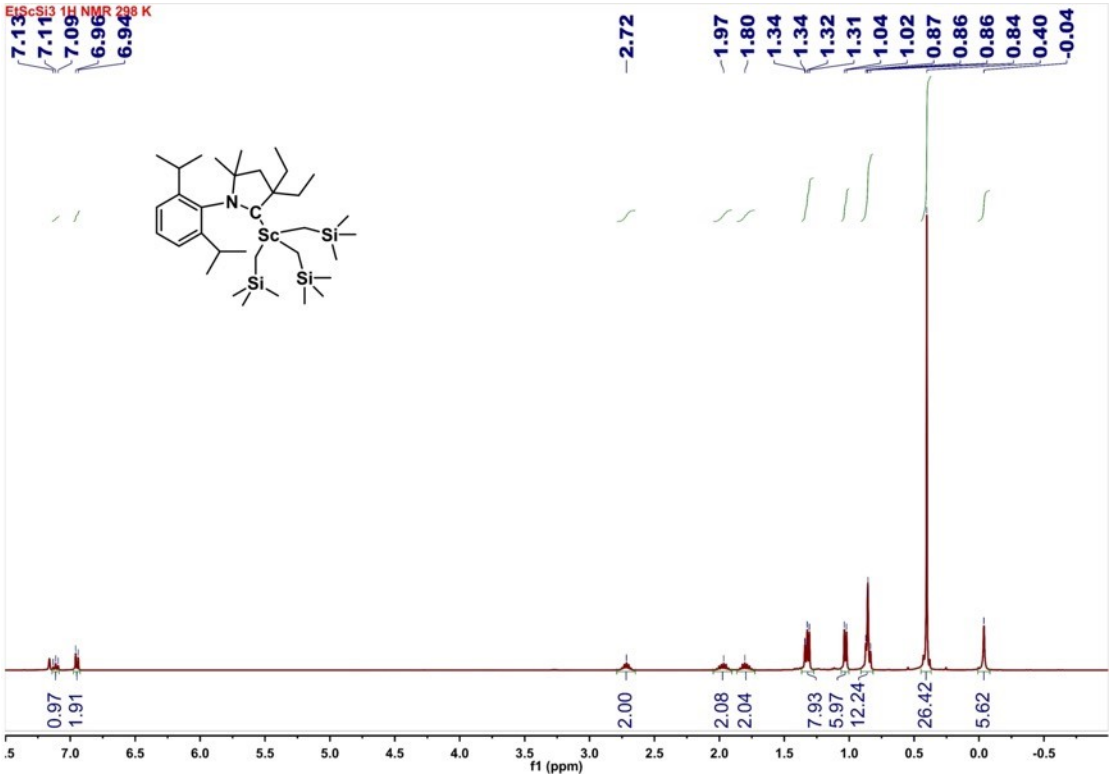



**Figure S15**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**2-Sc**) δ, ppm: 7.13 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C*H* of aryl), 6.96 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-C*H* of aryl), 2.72 (m, 2H, C*H*($CH_3$)$_2$), 1.97 and 1.80 (m, 4H, C$H_2$$CH_3$), 1.34 and 1.04 (m, 14 H, CH(C$H_3$)$_2$ and CC$H_2$), 0.87-0.84 (m, 12H, NC(C$H_3$)$_2$ and $CH_2$C$H_3$), 0.40 (s, 27H, Si(C$H_3$)$_3$) and -0.04 (s, 6H, C$H_2$Si($CH_3$)$_3$).

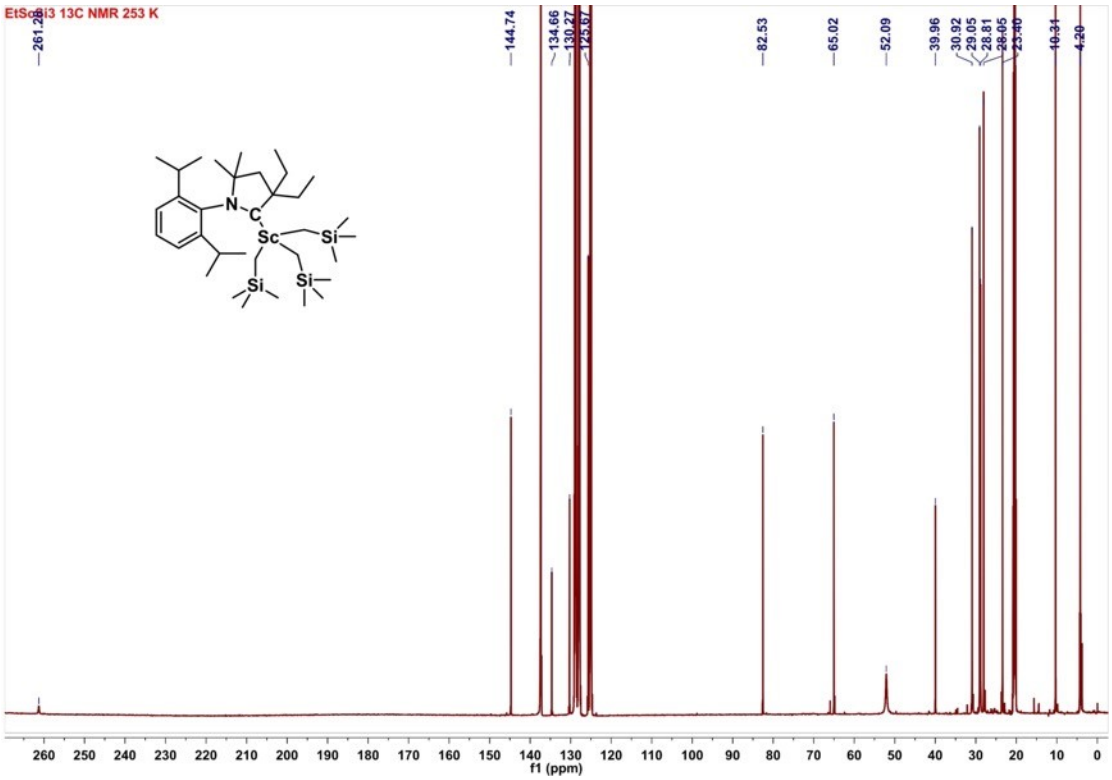



**Figure S16**. $^{13}C\{^{1}H\}$ NMR (151 MHz, $C_7D_8$, 253 K) spectrum of ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**2-Sc**) δ, ppm: 261.28 ($C_{carbene}$), 144.74, 134.66, 130.27, 125.67 (*C*H of aryl), 82.53 (N*C*($CH_3$)$_2$), 65.02 (C*C*$H_2$), 52.09 (*C*$H_2$Si($CH_3$)$_3$), 39.96 ($C_{carbene}$*C*($CH_3$)$_2$), 30.92, 29.05, 28.81, 28.05 (*C*$H_3$), 23.40 (*C*H($CH_3$)$_2$), 10.31 (*C*$H_2$CH$_3$), 4.20 (Si(*C*$H_3$)$_3$).

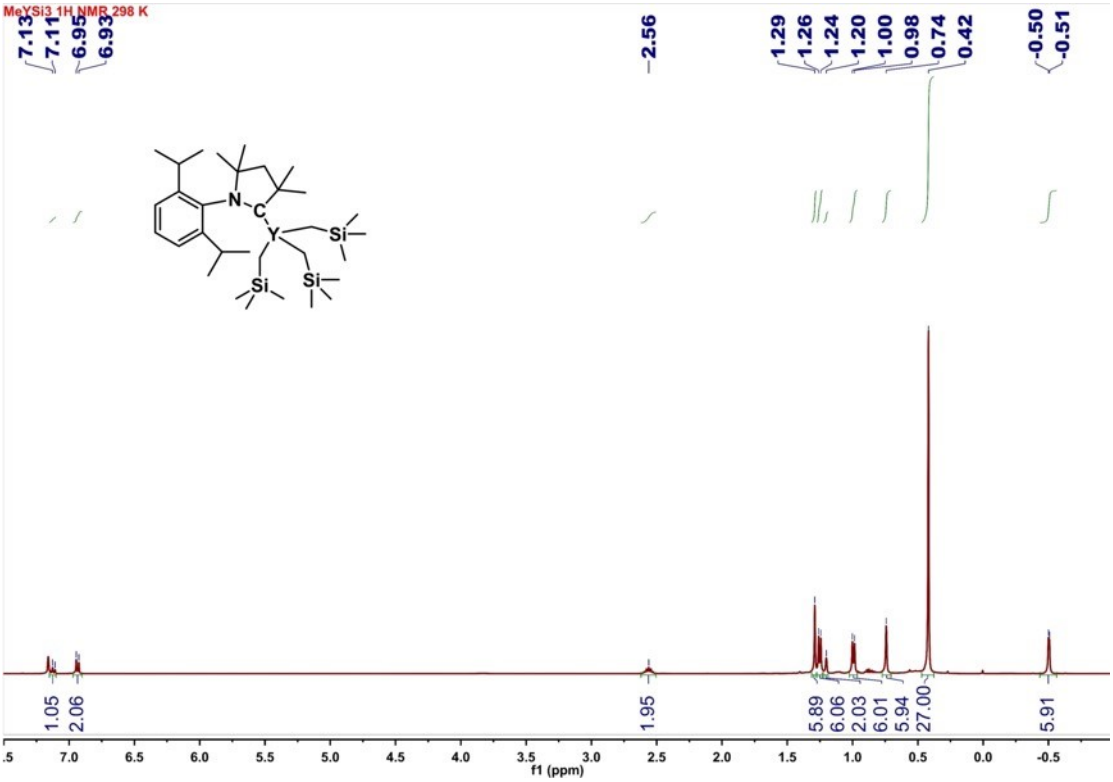



**Figure S17**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$ (**1-Y**) δ, ppm: 7.13 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C*H* of aryl), 6,95 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-C*H* of aryl), 2.56 (m, 2H, C*H*($CH_3$)$_2$), 1.29 and 0.74 (s, 12 H, NC(C*H*$_3$)$_2$ and CC*H*$_3$), 1.26 and 1.00 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, CH(C*H*$_3$)$_2$), 1.20 (s, 2H, CC*H*$_2$), 0.42 (s, 27H, Si(C*H*$_3$)$_3$) and -0.50 (d, $^{2}J_{YH}$ = 3.0 Hz, 6H, C*H*$_2$Si($CH_3$)$_3$).

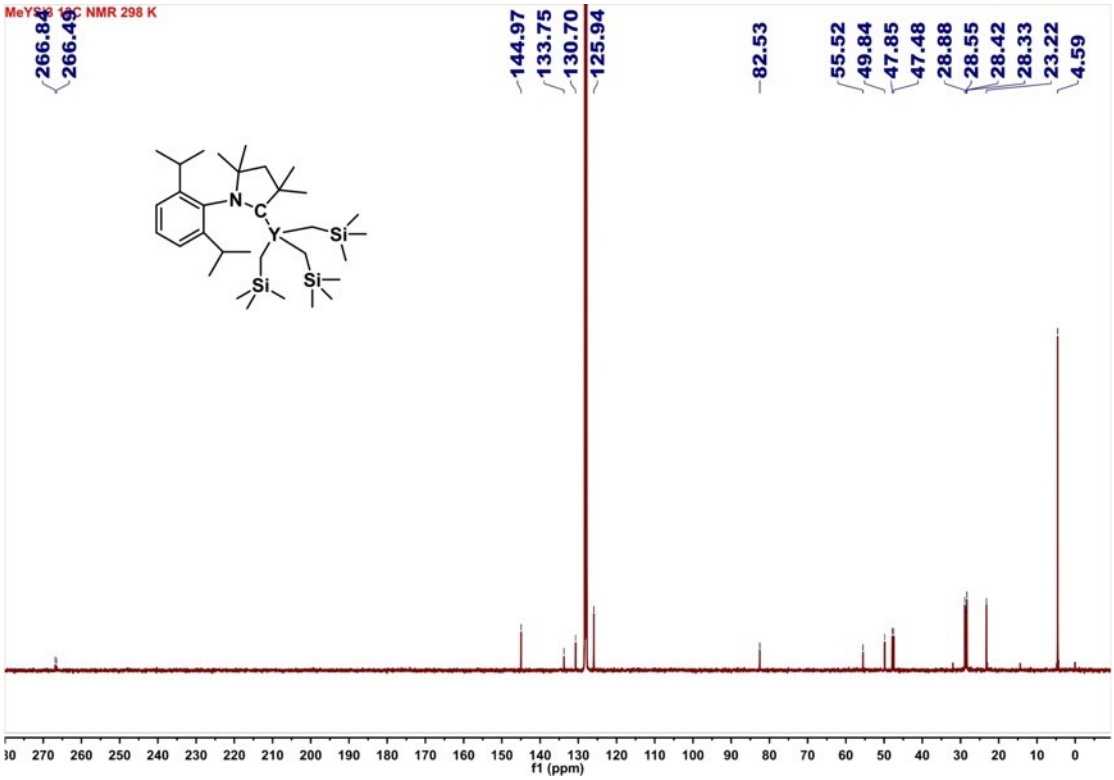



**Figure S18**. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$ (**1-Y**) δ, ppm: 266.66 ($C_{carbene}$, $^{1}J_{YC}$ = 35.4 Hz), 144.97, 133.75, 130.70, 125.94 (*C*H of aryl), 82.53 (N*C*(CH$_3$)$_2$), 55.52 (C*C*H$_2$), 49.84 ($C_{carbene}$*C*(CH$_3$)$_2$), 47.66 (*C*H$_2$Si(CH$_3$)$_3$, $^{1}J_{YC}$ = 37.1 Hz), 28.88, 28.55, 28.42, 28.33 (*C*H$_3$), 23.22 (*C*H(CH$_3$)$_2$), 4.59 (Si(*C*H$_3$)$_3$).

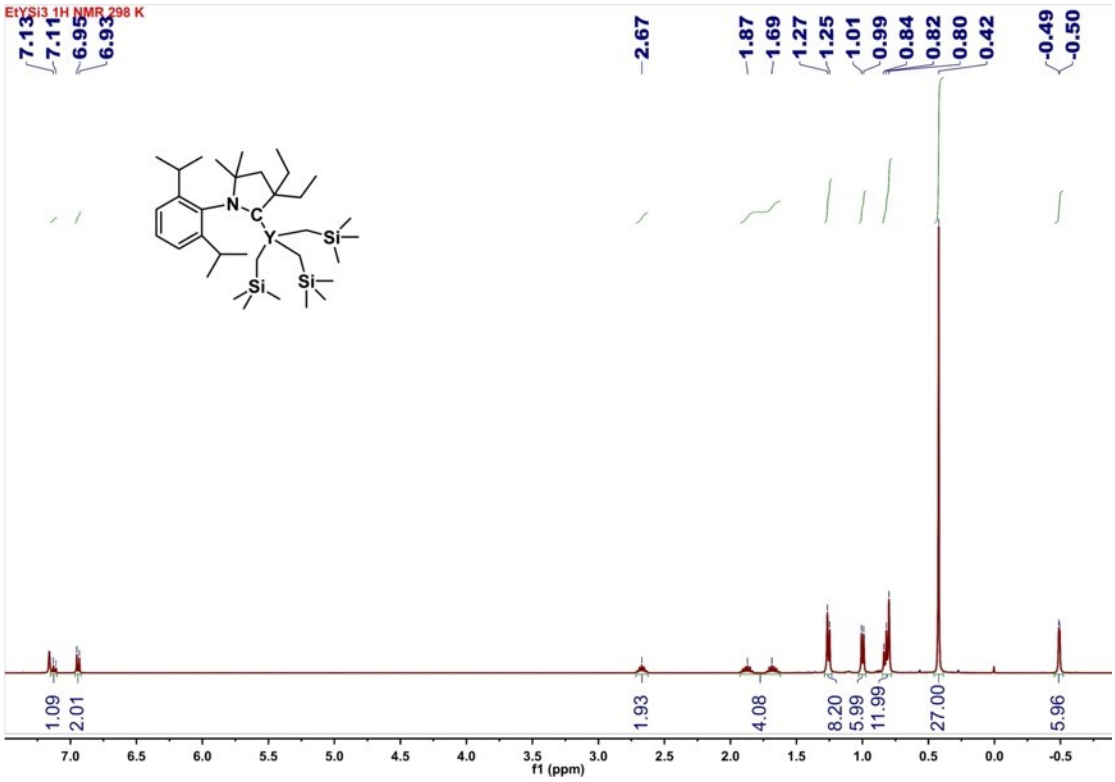



**Figure S19**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$ (**2-Y**) δ, ppm: 7.13 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C*H* of aryl), 6.95 (d, *J* = 7.8 Hz, 2H, *m*-C*H* of aryl), 2.67 (m, 2H, C*H*($CH_3$)$_2$), 1.87 and 1.69 (m, 4H, C$H_2$CH$_3$), 1.27 and 1.01 (m, 14 H, CH(C$H_3$)$_2$ and CC$H_2$), 0.84, 0.82 and 0.80 (m, 12H, NC(C$H_3$)$_2$ and $CH_2$C$H_3$), 0.42 (s, 27H, Si(C$H_3$)$_3$) and -0.49 (d, $^{3}J_{YH}$ = 3.0 Hz, 6H, C$H_2$Si($CH_3$)$_3$).

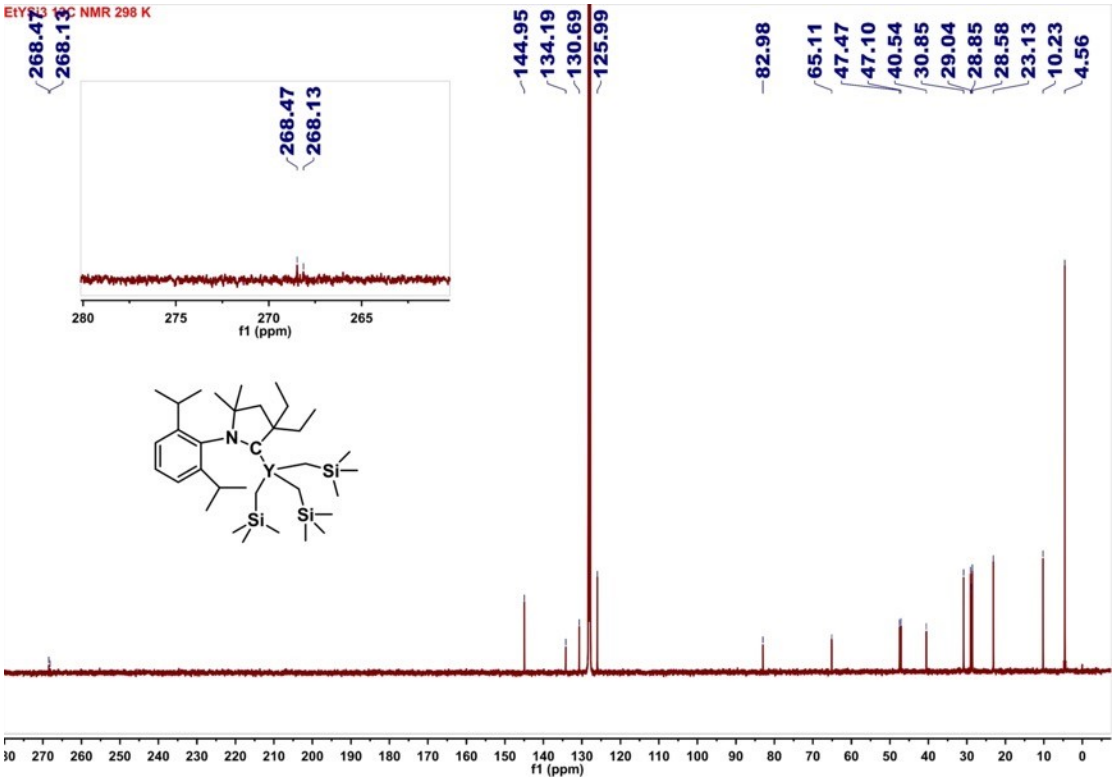



**Figure S20**. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K) spectrum of ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$ (**2-Y**) δ, ppm: 268.30 ($C_{carbene}$, $^{1}J_{YC}$ = 34.4 Hz), 144.95, 134.19, 130.69, 125.99 (*C*H of aryl), 82.98 (N*C*(CH$_3$)$_2$), 65.11 (C*C*H$_2$), 47.47, 47.10 (*C*H$_2$Si(CH$_3$)$_3$, $^{1}J_{YC}$ = 37.1 Hz), 40.54 ($C_{carbene}$*C*(CH$_3$)$_2$), 30.85, 29.04, 28.85, 28.58 (*C*H$_3$), 23.13 (*C*H(CH$_3$)$_2$), 10.23 (*C*H$_2$CH$_3$), 4.56 (Si(*C*H$_3$)$_3$).

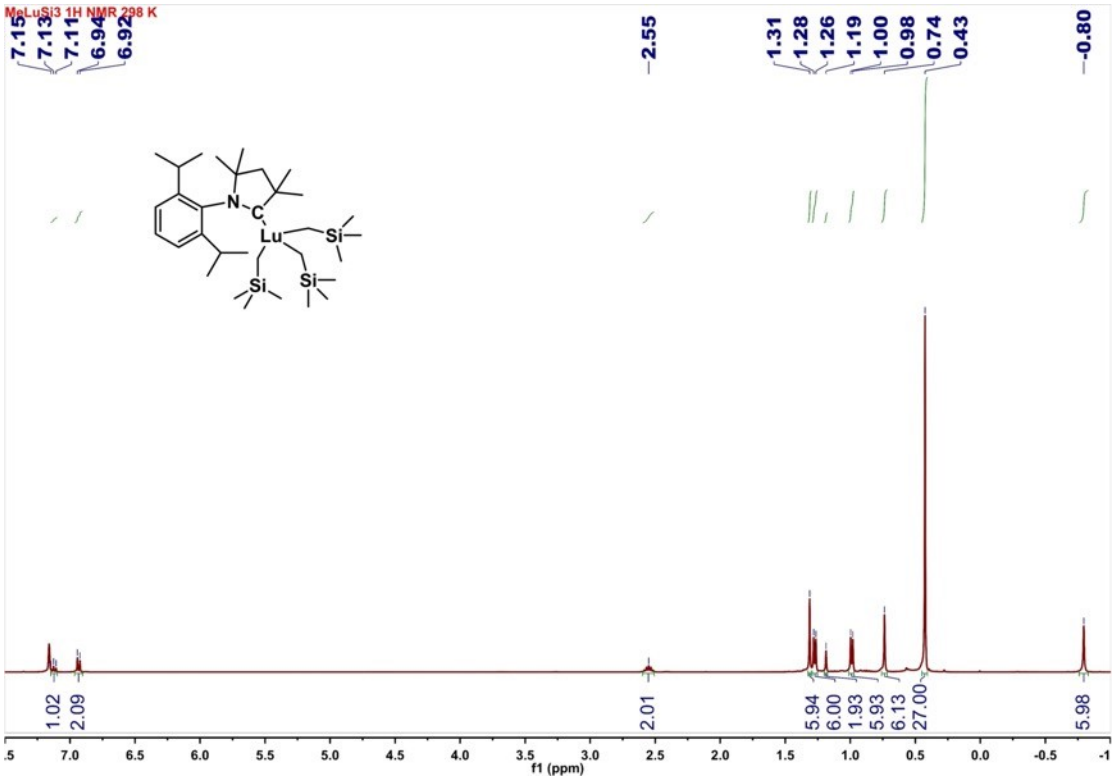



**Figure S21**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**1-Lu**) δ, ppm: 7.15 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C*H* of aryl), 6,94 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-C*H* of aryl), 2.55 (m, 2H, C*H*($CH_3$)$_2$), 1.31 and 0.74 (s, 12 H, NC($CH_3$)$_2$ and $C_{carbene}$C($CH_3$)$_2$), 1.28 and 1.00 (d, $^{3}J_{HH}$ = 6.7 Hz, 12H, CH($CH_3$)$_2$), 1.19 (s, 2H, $CH_2$), 0.43 (s, 27H, Si($CH_3$)$_3$) and -0.80 (s, 6H, $CH_2$Si($CH_3$)$_3$).

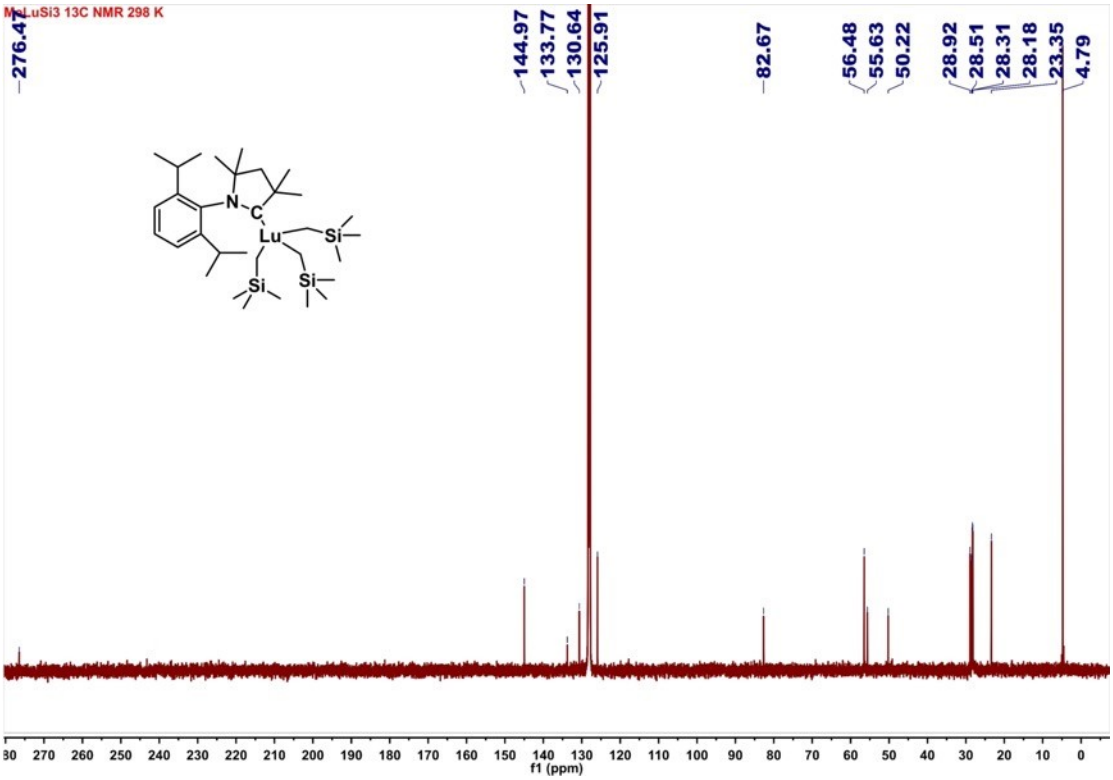



**Figure S22**. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**1-Lu**) δ, ppm: 276.47 ($C_{carbene}$), 144.97, 133.77, 130.64, 125.91 (*C*H of aryl), 82.67 (N*C*($CH_3$)$_2$), 56.48 (C*C*$H_2$), 55.63 (*C*$H_2$Si($CH_3$)$_3$), 50.22 ($C_{carbene}$*C*($CH_3$)$_2$), 28.92, 28.51, 28.31, 28.18 (*C*$H_3$), 23.35 (C*H*($CH_3$)$_2$), 4.79 (Si(*C*$H_3$)$_3$).

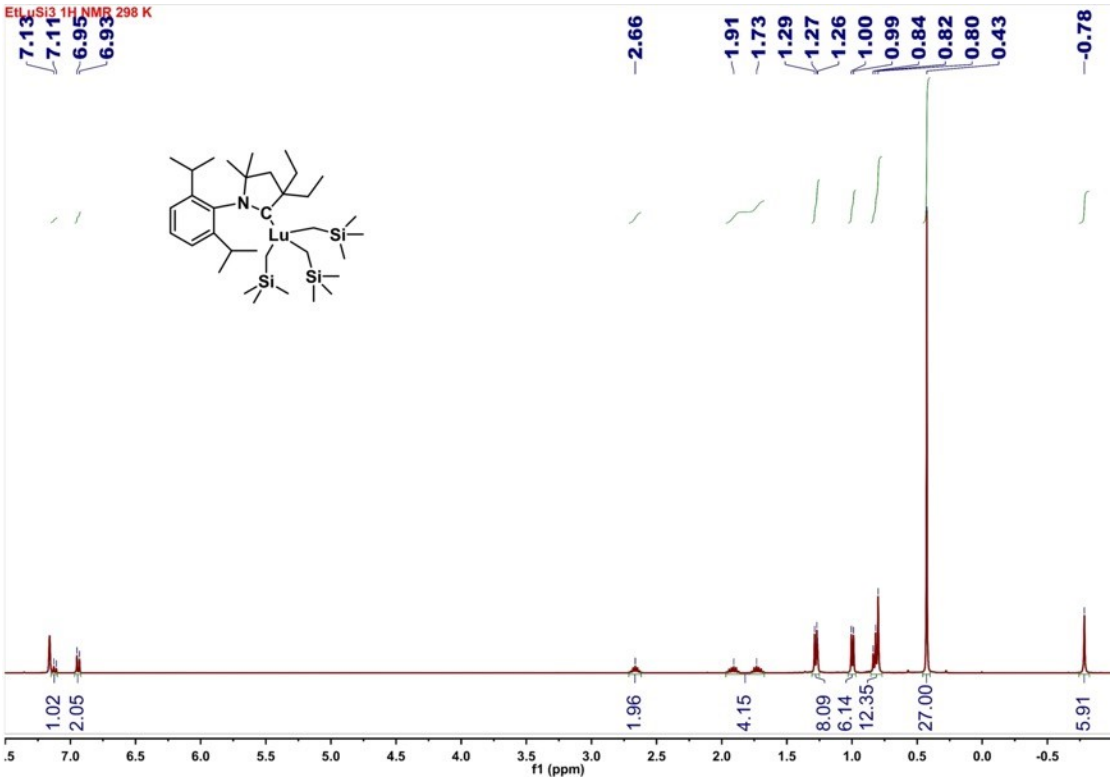



**Figure S23**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**2-Lu**) δ, ppm: 7.13 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H, *p*-C*H* of aryl), 6.95 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, *m*-C*H* of aryl), 2.66 (m, 2H, C*H*($CH_3$)$_2$), 1.91 and 1.73 (m, 4H, C$H_2$$CH_3$), 1.27 and 1.00 (m, 14 H, CH(C$H_3$)$_2$ and CC$H_2$), 0.84–0.80 (m, 12H, N(C$H_3$)$_2$ and $CH_2$C$H_3$), 0.43 (s, 27H, Si(C$H_3$)$_3$) and -0.78 (s, 6H, C$H_2$Si($CH_3$)$_3$).

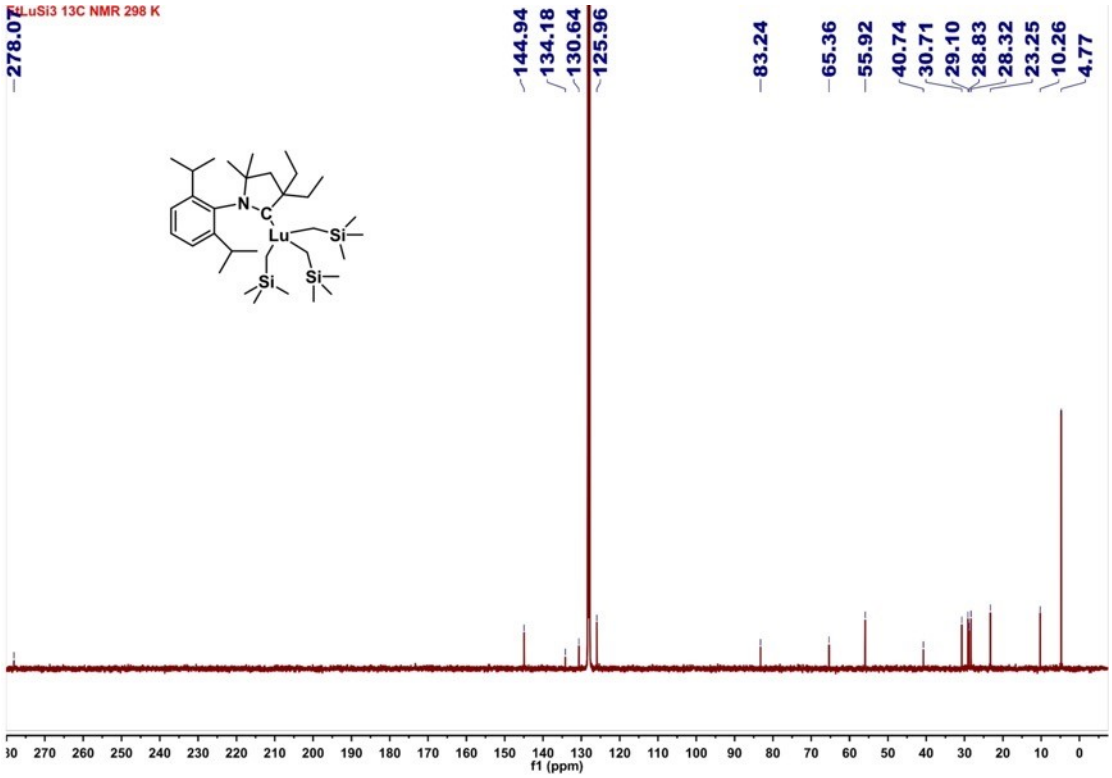



**Figure S24**. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K) spectrum of ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**2-Lu**) δ, ppm: 278.07 ($C_{carbene}$), 144.94, 134.18, 130.64, 125.96 (*C*H of aryl), 83.24 (N*C*(CH$_3$)$_2$), 65.36 (C*C*H$_2$), 55.92 (*C*H$_2$Si(CH$_3$)$_3$), 40.74 ($C_{carbene}$*C*(CH$_3$)$_2$), 30.71, 29.10, 28.83, 28.32 (*C*H$_3$), 23.25 (*C*H(CH$_3$)$_2$), 10.26 (*C*H$_2$CH$_3$), 4.77 (Si(*C*H$_3$)$_3$).

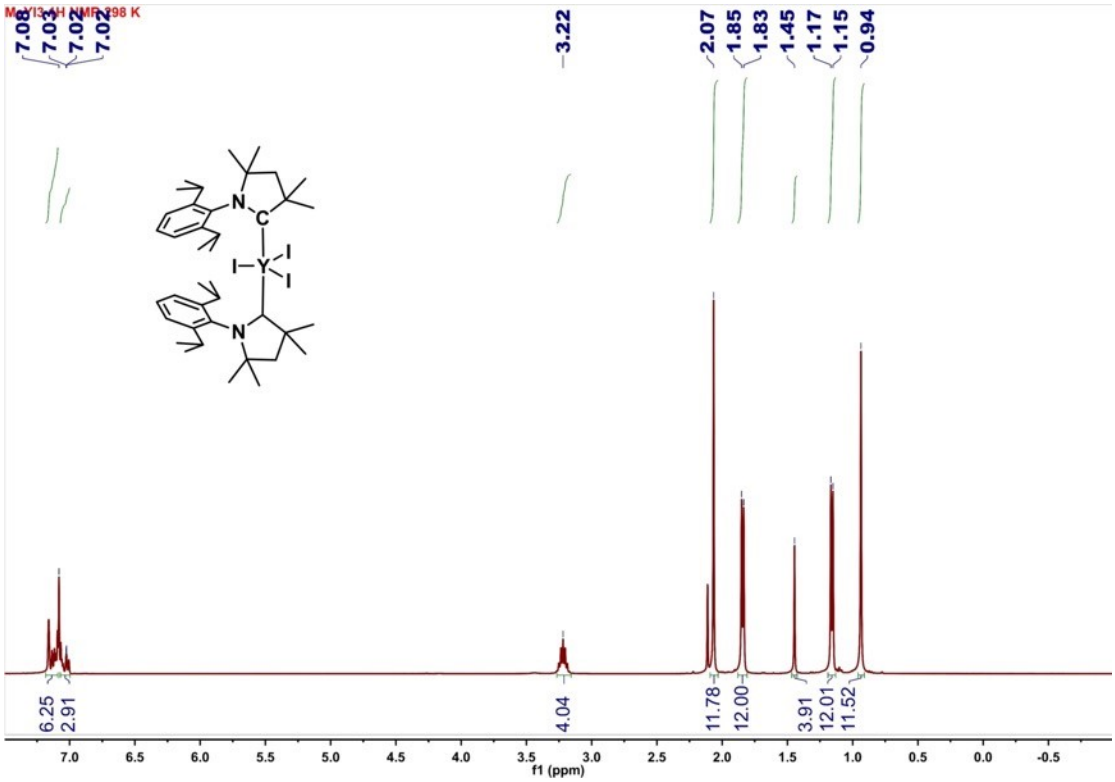



**Figure S25**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)$_2$YI$_3$ (**3-Y**) δ, ppm: 7.08 (m, 4H, C*H* of *m*-C*H* of aryl), 7.03 (m, 2H, *p*-C*H* of aryl), 3.22 (m, 4H, C*H*(CH$_3$)$_2$), 2.07 and 0.94 (s, 24H, NC(C*H*$_3$)$_2$ and C$_{carbene}$C(C*H*$_3$)$_2$), 1.85 and 1.17 (d, $^{3}J_{HH}$ = 6.4, 24H, CH(C*H*$_3$)$_2$) and 1.45 (s, 4H, C*H*$_2$).

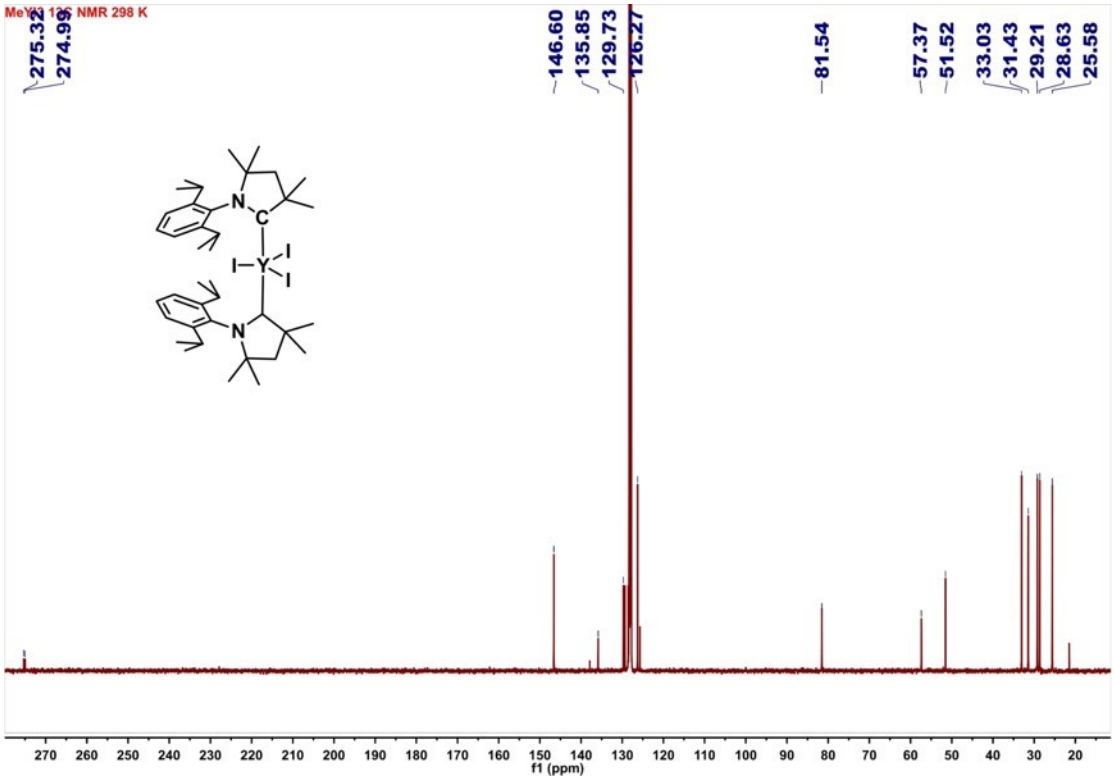



**Figure S26**. $^{13}C\{^{1}H\}$ NMR (126 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)$_2$YI$_3$ (**3-Y**) δ, ppm: 275.16 ($C_{carbene}$, $^{1}J_{YC}$ = 33.0 Hz), 146.60, 135.85, 129.73, 126.27 (*C*H of aryl), 81.54 (N*C*(CH$_3$)$_2$), 57.37 (*C*H$_2$), 51.52 (C$_{carbene}$*C*(CH$_3$)$_2$), 33.03 (C$_{carbene}$*C*(CH$_3$)$_2$), 31.43, 29.21, 28.63, 25.58 (*C*H$_3$).

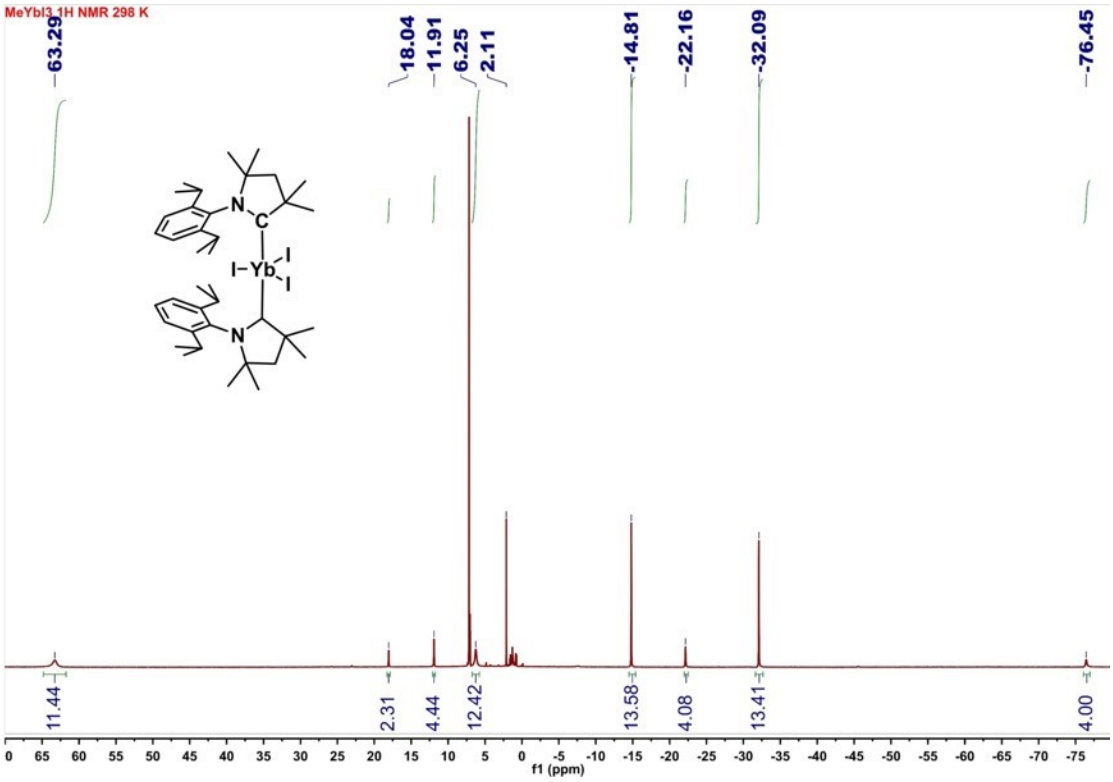



**Figure S27**. $^{1}$H NMR (400 MHz, $C_6D_6$, 298 K) spectrum of ($^{Me}$CAAC)$_2$YbI$_3$ (**3-Yb**) δ, ppm: 63.29 (12H, $C_{carbene}C(CH_3)_2$), 18.04 (2H, *p*-C*H* of aryl), 11.91 (4H, *m*-C*H* of aryl), 6.25 (12H, $NC(CH_3)_2$), -14.81 (12H, $CH(CH_3)_2$), -22.16 (4H, $CH_2$), -32.09 (12H, $CH(CH_3)_2$) and -76.45 (4H, $CH(CH_3)_2$).

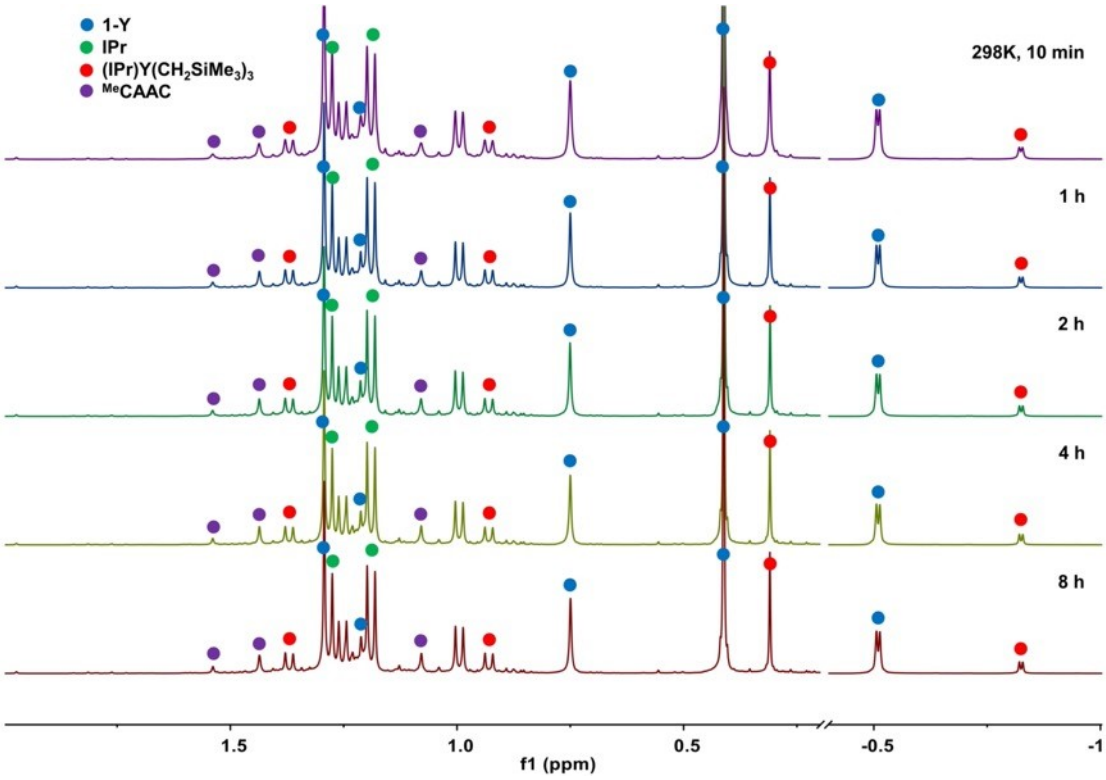



**Figure S28.** Monitoring the exchange reaction between **1-Y** (1.0 equiv.) and IPr (1.0 equiv.) in $C_6D_6$ by $^1$H NMR spectroscopy (400 MHz, 298K). Two representative regions (2.0 to 0.2 ppm and -0.4 to -1.0 ppm) were shown. The reaction reached equilibrium within 10 min after mixing and no significant change in $^1$H NMR spectra was observed after that. The ratio of **1-Y** vs. (IPr)Y($CH_2SiMe_3$)$_3$ is around 4:1.

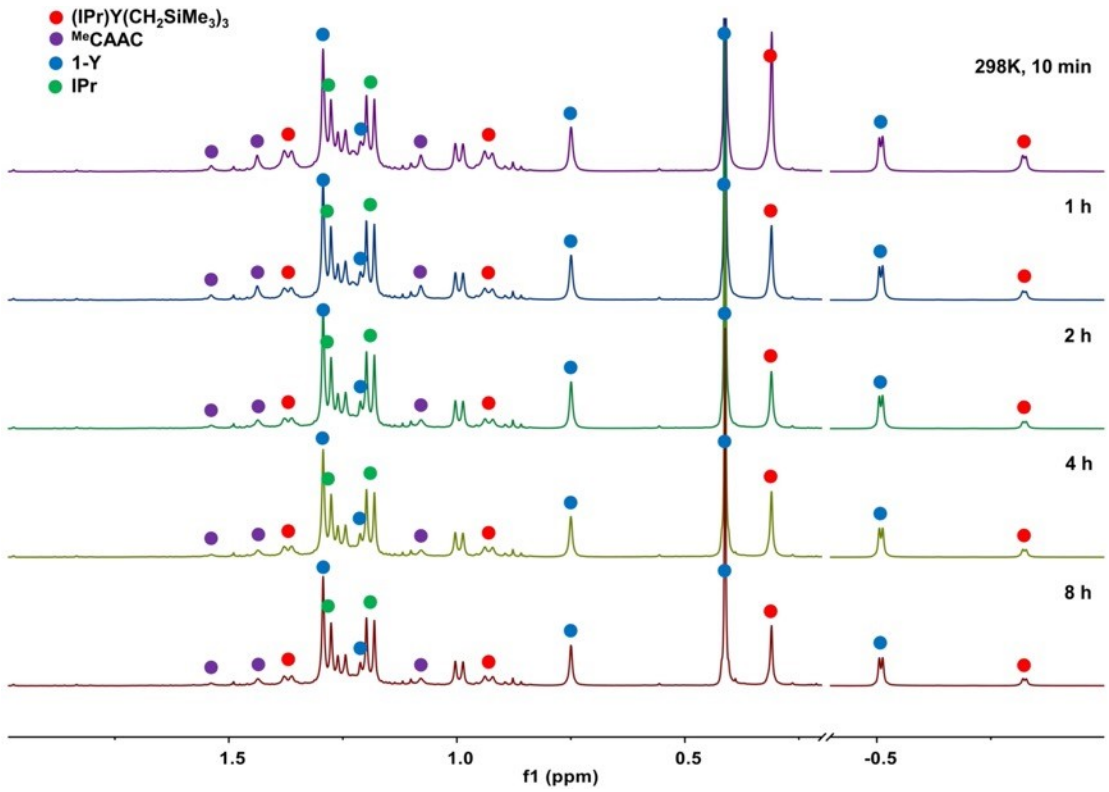



**Figure S29.** Monitoring the exchange reaction between (IPr)Y($CH_2SiMe_3$) (1.0 equiv.) and $^{Me}$CAAC (1.0 equiv.) in $C_6D_6$ by $^1$H NMR spectroscopy (400 MHz, 298K). Two representative regions (2.0 to 0.2 ppm and -0.4 to -1.0 ppm) were shown. The reaction reached equilibrium in 1 h after mixing and no significant change in $^1$H NMR spectra was observed after that. The ratio of **1-Y** vs. (IPr)Y($CH_2SiMe_3$)$_3$ is around 4:1.

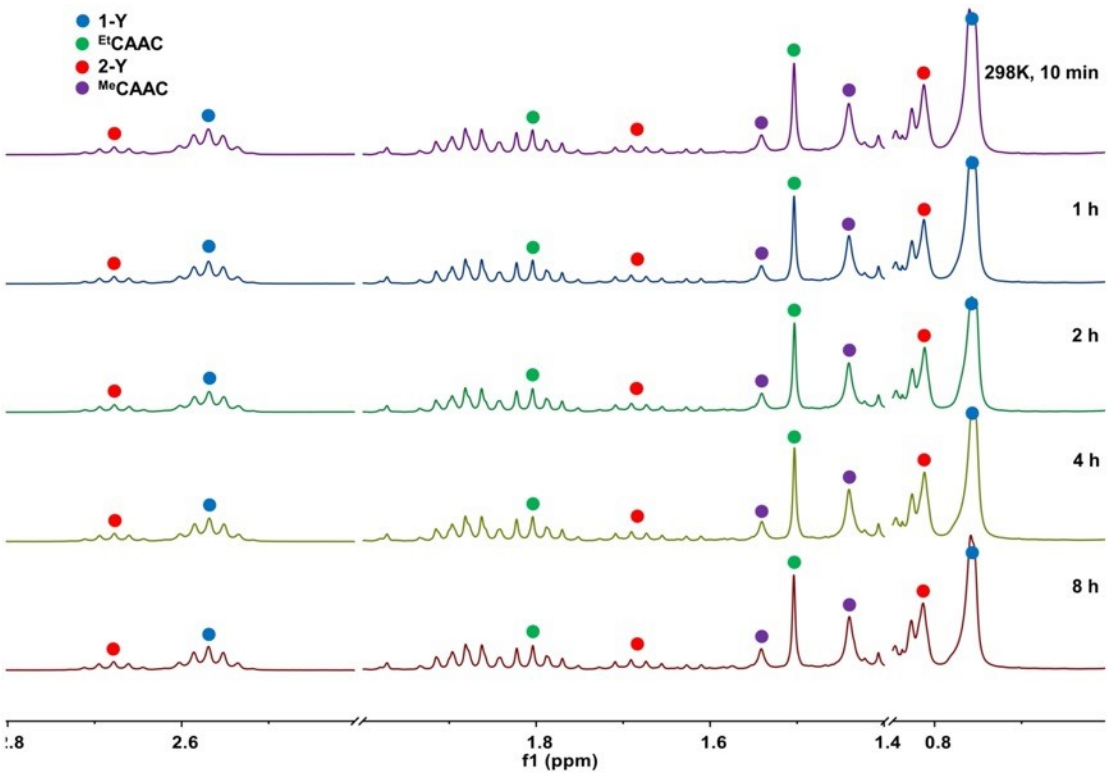



**Figure S30.** Monitoring the exchange reaction between **1-Y** (1.00 equiv.) and $^{Et}$CAAC (0.82 equiv.) in $C_6D_6$ by $^1$H NMR spectroscopy (400 MHz, 298K). Three representative regions (2.80 to 2.40 ppm, 2.00 to 1.40 ppm and 0.85 to 0.60 ppm) were shown. The reaction reached equilibrium in 10 min after mixing and no significant change in $^1$H NMR spectra was observed after that. The ratio of **1-Y** : $^{Et}$CAAC : **2-Y** : $^{Me}$CAAC is ca. 5:4:2:2, which leads to an equilibrium constant: $K$ = ([**2-Y**][$^{Me}$CAAC])/([**1-Y**][$^{Et}$CAAC]) = 1/5.

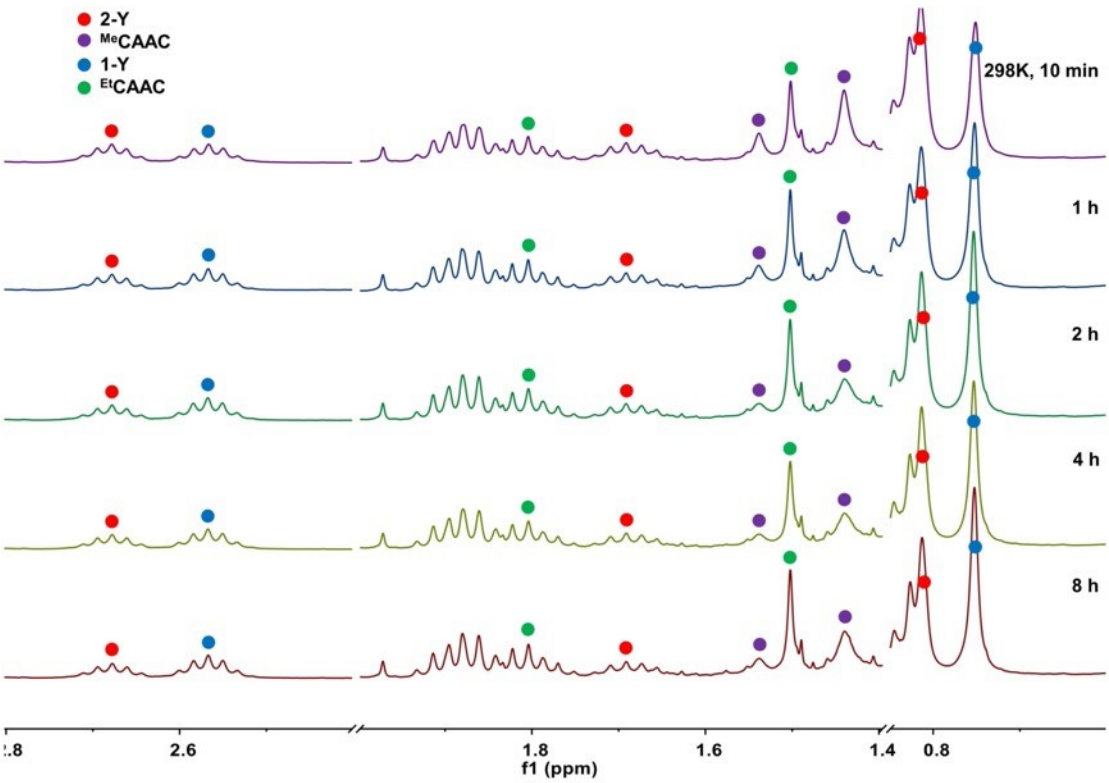


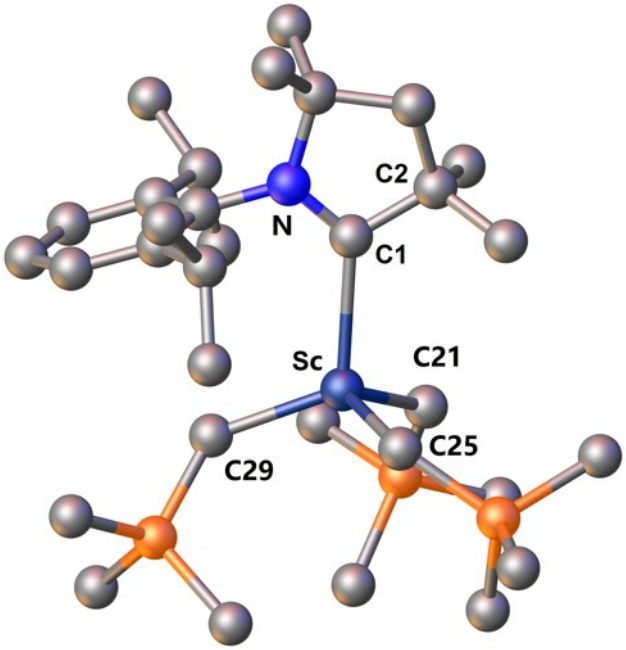

**Figure S31.** Monitoring the exchange reaction between **2-Y** (1.0 equiv.) and $^{Me}$CAAC (0.81 equiv.) in $C_6D_6$ by $^1$H NMR spectroscopy (400 MHz, 298K). Three representative regions (2.80 to 2.40 ppm, 2.00 to 1.40 ppm and 0.85 to 0.60 ppm) were shown. The reaction reached equilibrium in 2 h after mixing and no significant change in $^1$H NMR spectra was observed after that. The ratio of **2-Y** : $^{Me}$CAAC : **1-Y** : $^{Et}$CAAC is ca. 3:2:5:6, which leads to an equilibrium constant: $K$ = ([**2-Y**][$^{Me}$CAAC])/([**1-Y**][$^{Et}$CAAC]) = 1/5.

# 3. Density Functional Theory (DFT) Calculations

## Computational Methods.

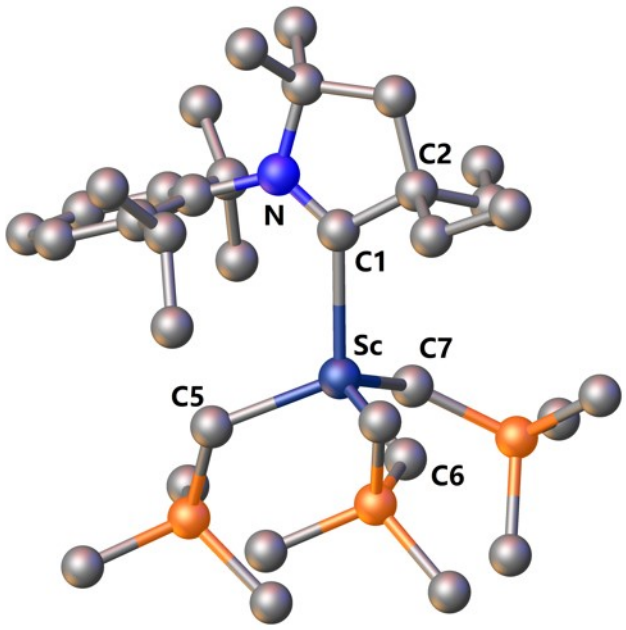
DFT calculations were performed for the closed-shell systems, ($^{R}$CAAC)M($CH_2SiMe_3$)$_3$ (R = Me, Et, M = Sc, Y and Lu) and ($^{Me}$CAAC)$_2$YI$_3$, with ORCA v. 4.2.0,[3, 4] starting from the corresponding single crystal structures. Triple-zeta plus polarization Ahlrichs basis sets (def2-TZVP) were utilized for the calculation with scalar relativistic effects taken into account,[5-8] and segmented all-electron relativistically contracted (SARC) basis set was chosen for Lu.[9] With the PBE functional, geometry optimization was converged to energetic minima, as confirmed by frequency analysis.[10] Single-point calculations were based on the optimized structures with the hybrid functional PBE0 and the TZVPP basis sets.[5, 11] The RI (resolution of the identity) acceleration was turned on to speed up the DFT calculations.[12, 13] Tighter than default SCF (“TightSCF”), dispersion correction ("D3BJ") and finer grid (“Grid6”) were specified as well.[14, 15] The molecular orbitals (MOs) are visualized by VMD v. 1.9.3,[16] combined with the wave function analysis program Multiwfn.[17] The orbital isovalue of 0.05 is used for all plots.

**Table S1.** Comparison of crystallographic and optimized structures of ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**1-Sc**).



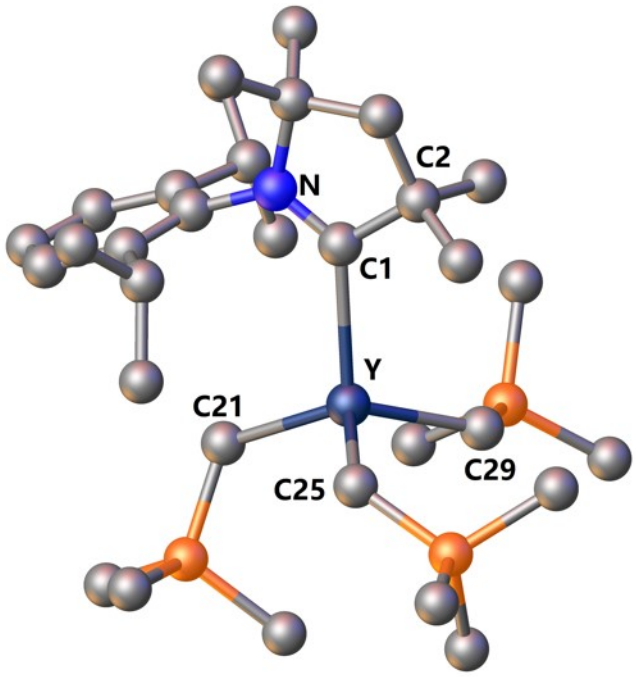

| Selected distances [Å] and angles [°] | Experimental | Calculated | Difference |
|---|---|---|---|
| **C1–N** | 1.305(2) | 1.314 | 0.009 |
| **C1–C2** | 1.525(2) | 1.522 | -0.003 |
| **Sc–C1** | 2.445(1) | 2.449 | 0.004 |
| **Sc–C21** | 2.213(1) | 2.212 | -0.001 |
| **Sc–C25** | 2.222(1) | 2.221 | -0.001 |
| **Sc–C29** | 2.222(2) | 2.218 | -0.004 |
| **Avg. Sc–$C_{alkyl}$** | 2.219 | 2.217 | -0.002 |
| **C1–Sc–C21** | 114.54(5) | 114.4 | -0.1 |
| **C1–Sc–C25** | 105.14(5) | 101.5 | -3.6 |
| **C1–Sc–C29** | 106.98(5) | 105.3 | -1.7 |
| **C21–Sc–C25** | 111.15(6) | 113.9 | 2.7 |
| **C21–Sc–C29** | 111.11(6) | 110.0 | -1.1 |
| **C25–Sc–C29** | 107.48(5) | 111.3 | 3.8 |

**Table S2.** Comparison of crystallographic and optimized structures of ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**2-Sc**).



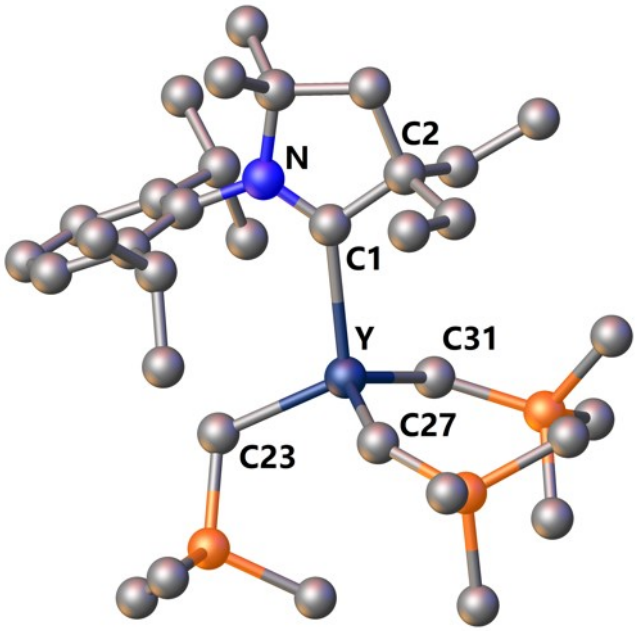

| Selected distances [Å] and angles [°] | Experimental | Calculated | Difference |
|---|---|---|---|
| **C1–N** | 1.296(3) | 1.312 | 0.016 |
| **C1–C2** | 1.526(3) | 1.514 | -0.012 |
| **Sc–C1** | 2.455(2) | 2.443 | -0.012 |
| **Sc–C5** | 2.199(3) | 2.220 | 0.021 |
| **Sc–C6** | 2.261(5) | 2.213 | -0.048 |
| **Sc–C7** | 2.225(3) | 2.211 | -0.014 |
| **Avg. Sc–C$_{alkyl}$** | 2.228 | 2.215 | -0.013 |
| **C1–Sc–C5** | 114.2(1) | 113.2 | -1.0 |
| **C1–Sc–C6** | 109.0(1) | 106.9 | -2.1 |
| **C1–Sc–C7** | 108.1(1) | 111.5 | 3.4 |
| **C5–Sc–C6** | 117.7(2) | 110.8 | -6.9 |
| **C5–Sc–C7** | 108.2(1) | 106.1 | -2.1 |
| **C6–Sc–C7** | 98.1(2) | 108.3 | 10.2 |

**Table S3.** Comparison of crystallographic and optimized structures of ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$ (**1-Y**).



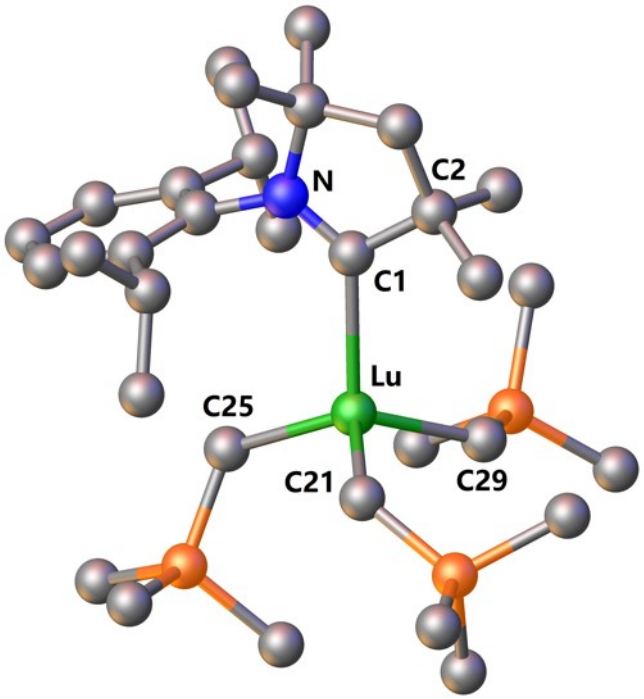

| Selected distances [Å] and angles [°] | Experimental | Calculated | Difference |
|---|---|---|---|
| **C1–N** | 1.297(5) | 1.312 | 0.015 |
| **C1–C2** | 1.516(5) | 1.517 | 0.001 |
| **Y–C1** | 2.579(3) | 2.581 | 0.002 |
| **Y–C21** | 2.363(4) | 2.381 | 0.018 |
| **Y–C25** | 2.381(4) | 2.380 | -0.001 |
| **Y–C29** | 2.354(4) | 2.382 | 0.028 |
| **Avg. Y–$C_{alkyl}$** | 2.366 | 2.381 | 0.015 |
| **C1–Y–C21** | 111.0(1) | 110.7 | -0.3 |
| **C1–Y–C25** | 107.9(1) | 104.7 | -3.2 |
| **C1–Y–C29** | 110.7(1) | 109.2 | -1.5 |
| **C21–Y–C25** | 113.1(1) | 111.3 | -1.8 |
| **C21–Y–C29** | 110.3(1) | 113.3 | 3.0 |
| **C25–Y–C29** | 103.7(1) | 107.2 | 3.5 |

**Table S4.** Comparison of crystallographic and optimized structures of ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$ (**2-Y**).



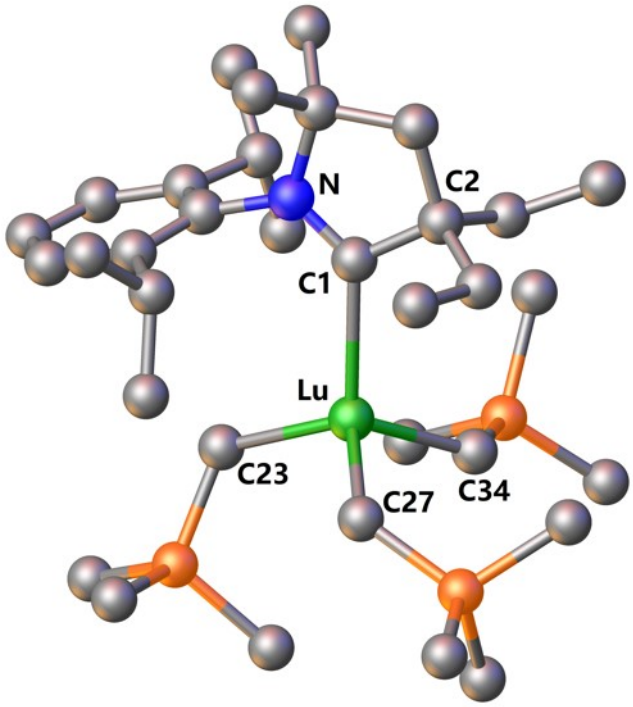

| **Selected distances [Å] and angles [°]** | **Experimental** | **Calculated** | **Difference** |
|---|---|---|---|
| **C1–N** | 1.298(3) | 1.311 | 0.013 |
| **C1–C2** | 1.516(3) | 1.515 | -0.001 |
| **Y–C1** | 2.596(2) | 2.581 | -0.015 |
| **Y–C23** | 2.373(3) | 2.377 | 0.004 |
| **Y–C27** | 2.379(3) | 2.374 | -0.005 |
| **Y–C31** | 2.387(3) | 2.392 | 0.005 |
| **Avg. Y–$C_{alkyl}$** | 2.380 | 2.381 | 0.001 |
| **C1–Y–C23** | 117.55(9) | 112.0 | -5.6 |
| **C1–Y–C27** | 103.12(8) | 101.4 | -1.7 |
| **C1–Y–C31** | 105.09(9) | 106.8 | 1.7 |
| **C23–Y–C27** | 111.42(9) | 107.6 | -3.8 |
| **C23–Y–C31** | 108.2(1) | 104.8 | -3.4 |
| **C27–Y–C31** | 111.2(1) | 124.2 | 13.0 |

**Table S5.** Comparison of crystallographic and optimized structures of ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**1-Lu**).



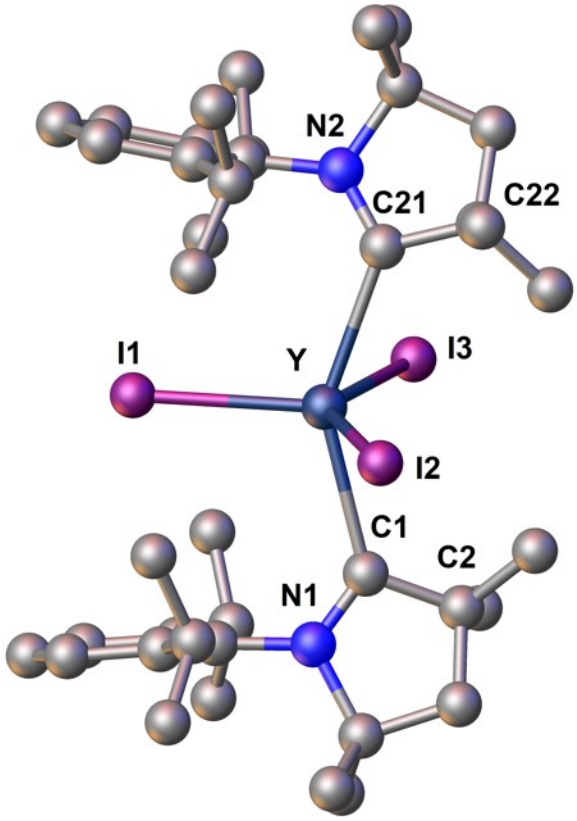

| Selected distances [Å] and angles [°] | Experimental | Calculated | Difference |
|---|---|---|---|
| **C1–N** | 1.302(4) | 1.305 | 0.003 |
| **C1–C2** | 1.525(4) | 1.515 | -0.010 |
| **Lu–C1** | 2.530(3) | 2.515 | -0.015 |
| **Lu–C21** | 2.332(3) | 2.318 | -0.014 |
| **Lu–C25** | 2.323(3) | 2.318 | -0.005 |
| **Lu–C29** | 2.340(3) | 2.318 | -0.022 |
| **Avg. Lu–$C_{alkyl}$** | 2.332 | 2.318 | -0.014 |
| **C1–Lu–C21** | 105.7(1) | 103.9 | -1.8 |
| **C1–Lu–C25** | 113.6(1) | 112.3 | -1.3 |
| **C1–Lu–C29** | 110.1(1) | 110.1 | 0 |
| **C21–Lu–C25** | 107.6(1) | 111.3 | 3.7 |
| **C21–Lu–C29** | 109.1(1) | 107.7 | -1.4 |
| **C25–Lu–C29** | 110.5(1) | 111.3 | 0.8 |

**Table S6.** Comparison of crystallographic and optimized structures of ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**2-Lu**).




| Selected distances [Å] and angles [°] | Experimental | Calculated | Difference |
|---|---|---|---|
| **C1–N** | 1.296(3) | 1.311 | 0.015 |
| **C1–C2** | 1.521(3) | 1.514 | -0.007 |
| **Lu–C1** | 2.539(2) | 2.515 | -0.024 |
| **Lu–C23** | 2.321(3) | 2.313 | -0.008 |
| **Lu–C27** | 2.326(2) | 2.320 | -0.006 |
| **Lu–C34** | 2.317(3) | 2.314 | -0.003 |
| **Avg. Lu–$C_{alkyl}$** | 2.321 | 2.316 | -0.005 |
| **C1–Lu–C23** | 116.86(9) | 111.7 | -5.2 |
| **C1–Lu–C27** | 105.60(8) | 108.9 | 3.3 |
| **C1–Lu–C34** | 103.89(8) | 112.6 | 8.7 |
| **C23–Lu–C27** | 108.2(1) | 109.7 | 1.5 |
| **C23–Lu–C34** | 111.0(1) | 108.5 | -2.5 |
| **C27–Lu–C34** | 111.22(9) | 105.2 | -6.0 |

**Table S7.** Comparison of crystallographic and optimized structures of $(^{Me}CAAC)_2YI_3$ (**3-Y**).




| Selected distances [Å] and angles [°] | Experimental | Calculated | Difference |
|---|---|---|---|
| **C21–N2** | 1.312(5) | 1.325 | 0.013 |
| **C21–C22** | 1.535(5) | 1.535 | 0 |
| **C1–N1** | 1.309(5) | 1.325 | 0.016 |
| **C1–C2** | 1.541(6) | 1.536 | -0.005 |
| **Y–C21** | 2.623(4) | 2.591 | -0.032 |
| **Y–C1** | 2.639(4) | 2.590 | -0.049 |
| **Y–I1** | 2.8583(5) | 2.876 | 0.018 |
| **Y–I2** | 2.9614(5) | 2.954 | -0.007 |
| **Y–I3** | 2.9359(5) | 2.954 | 0.018 |
| **Avg. Y–I** | 2.9185 | 2.928 | 0.010 |
| **C21–Y–I1** | 101.45(8) | 106.5 | 5.1 |
| **C21–Y–I2** | 79.35(8) | 77.8 | -1.6 |
| **C21–Y–I3** | 91.57(8) | 90.1 | -1.5 |
| **C1–Y–I1** | 103.25(9) | 107.0 | 3.9 |
| **C1–Y–I2** | 88.66(9) | 89.7 | 1.0 |
| **C1–Y–I3** | 84.52(9) | 77.8 | -6.7 |
| **I1–Y–I2** | 111.69(2) | 112.0 | 0.3 |
| **I1–Y–I3** | 106.27(2) | 111.2 | 4.9 |
| **I2–Y–I3** | 141.98(2) | 136.8 | -5.2 |

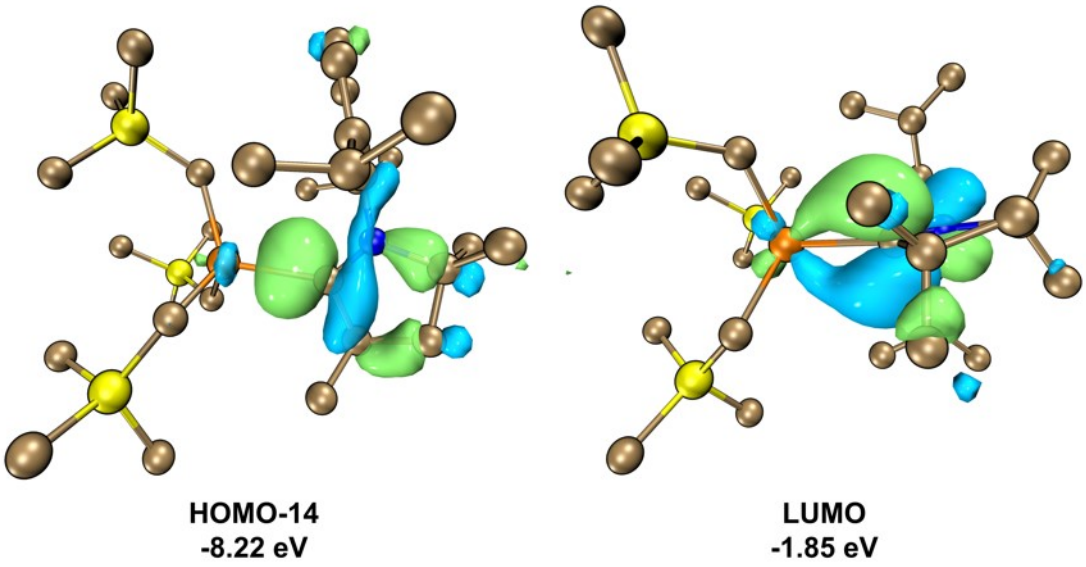



**Figure S32.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Sc and the carbene for ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**1-Sc**). Hydrogen atoms are omitted for clarity. Representations: Sc, orange; Si, yellow; N, blue; C, brown.

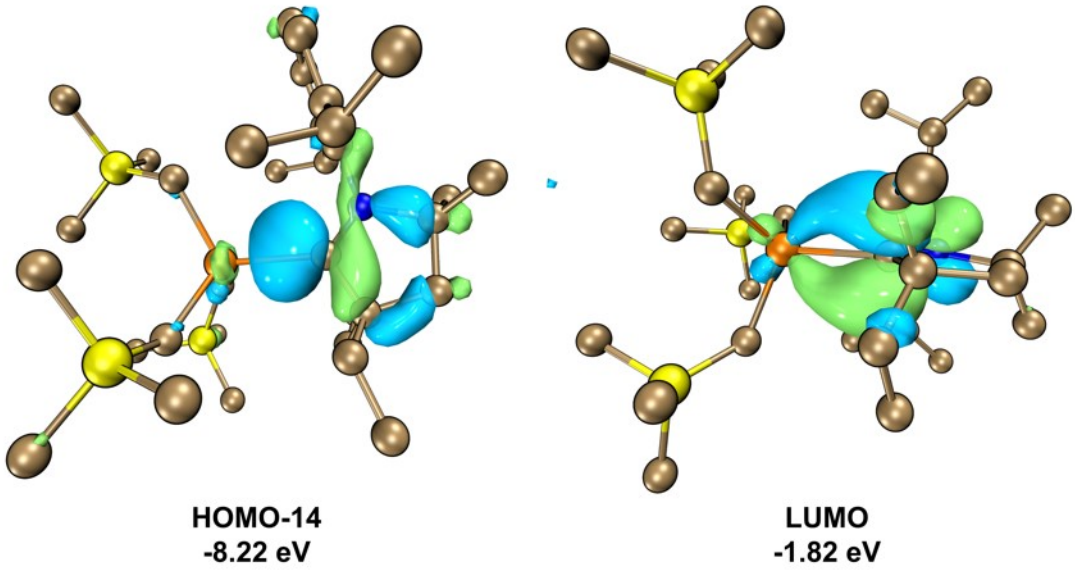



**Figure S33.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Sc and the carbene for ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$ (**2-Sc**). Hydrogen atoms are omitted for clarity. Representations: Sc, orange; Si, yellow; N, blue; C, brown.

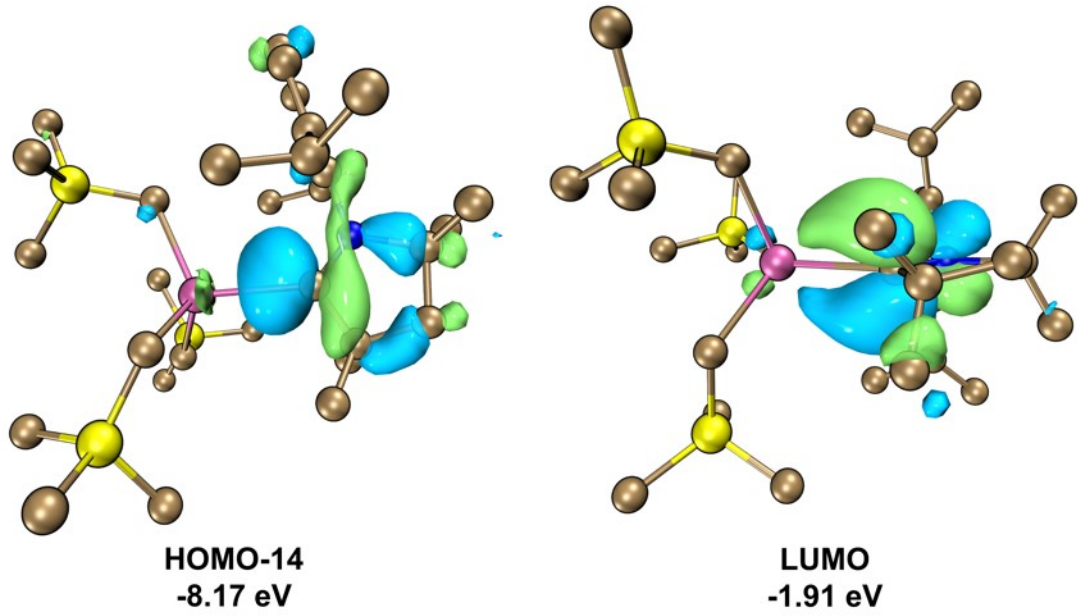



**Figure S34.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Y and the carbene for ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$ (**1-Y**). Hydrogen atoms are omitted for clarity. Representations: Y, pink; Si, yellow; N, blue; C, brown.

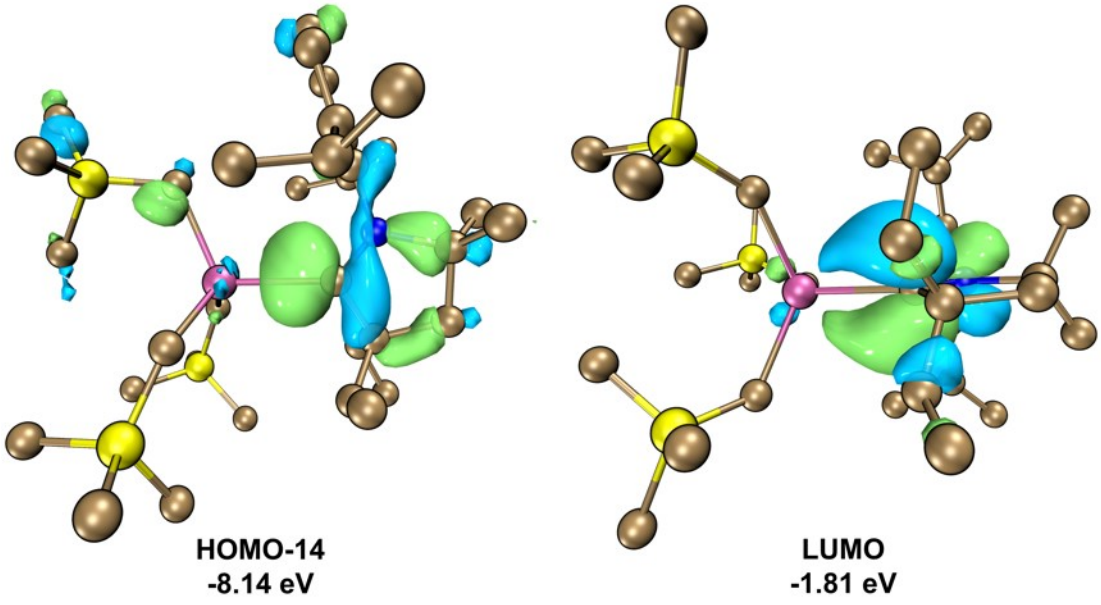



**Figure S35.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Y and the carbene for ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$ (**2-Y**). Hydrogen atoms are omitted for clarity. Representations: Y, pink; Si, yellow; N, blue; C, brown.

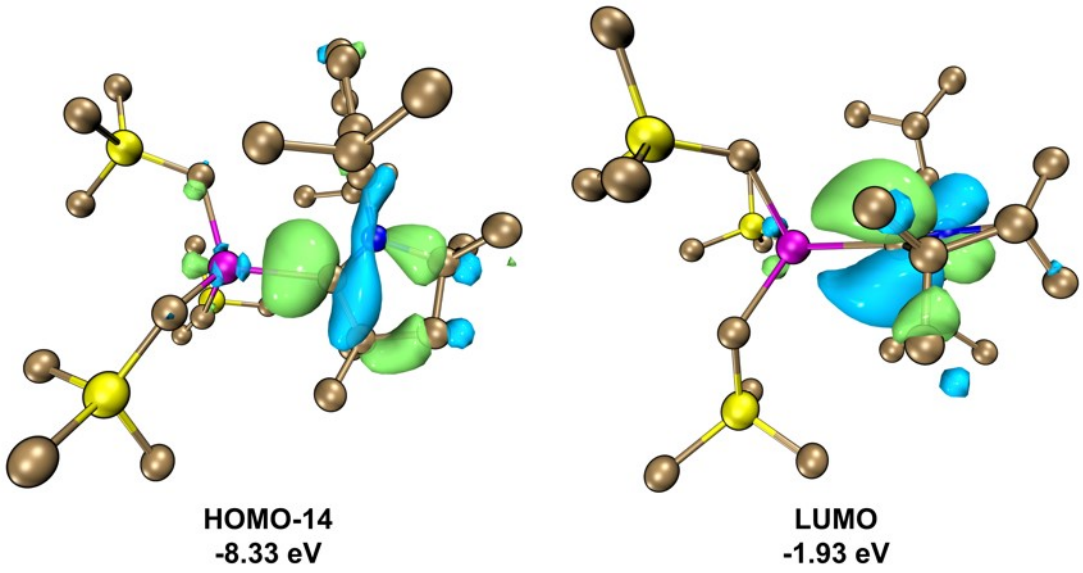



**Figure S36.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Lu and the carbene for ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**1-Lu**). Hydrogen atoms are omitted for clarity. Representations: Lu, purple; Si, yellow; N, blue; C, brown.

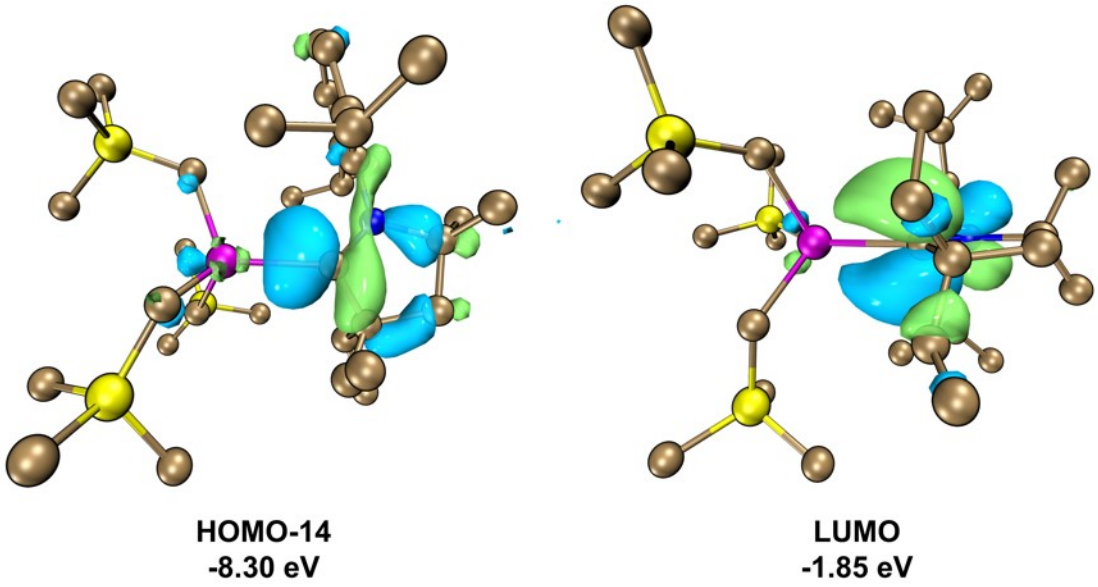



**Figure S37.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Lu and the carbene for ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$ (**2-Lu**). Hydrogen atoms are omitted for clarity. Representations: Lu, purple; Si, yellow; N, blue; C, brown.

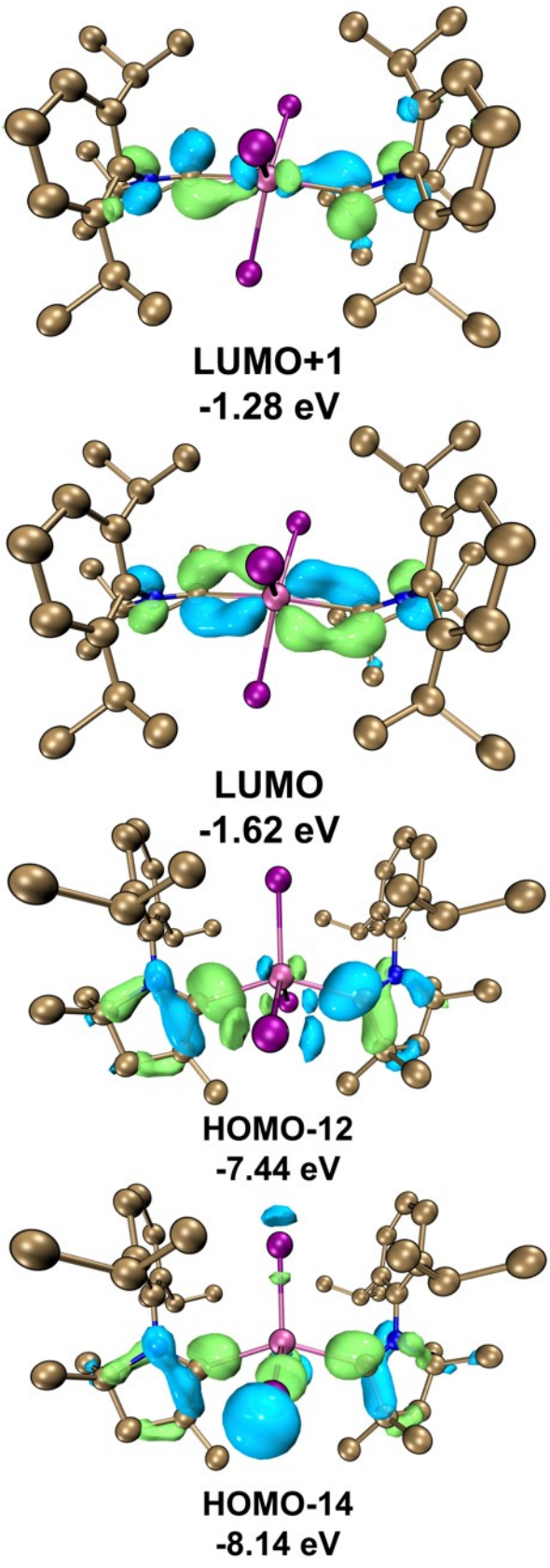



**Figure S38.** Selected molecular orbitals (isovalue = 0.05) that represent the interaction between Y and the carbenes for ($^{Me}$CAAC)$_2$YI$_3$ (**3-Y**). Hydrogen atoms are omitted for clarity. Representations:

Y, pink; I, purple; N, blue; C, brown.

**Table S8.** Composition analysis of the molecular orbitals (HOMO-14) reflecting σ donation from the lone pair of the carbene to the rare-earth metal ion in ($^{R}$CAAC)M($CH_2SiMe_3$)$_3$ (R = Me and Et, M = Sc, Y and Lu).

| **($^{R}$CAAC)M($CH_2SiMe_3$)$_3$** | | **Sc** | **Y** | **Lu** |
|---|---|---|---|---|
| **R = Me** | **Metal (%)** | 4.1<br>(1.5 s, 0.6 p, 1.9 d) | 11.7<br>(6.7 s, 2.0 p, 2.7 d) | 15.5<br>(9.5 s, 1.8 p, 2.6 d, 1.6 f) |
| | **Carbene (%)** | 46.5<br>(8.0 s, 37.9 p) | 40.0<br>(7.7 s, 31.9 p) | 38.8<br>(6.5 s, 32.0 p) |
| | **Nitrogen (%)** | 3.8<br>(3.8 p) | 3.6<br>(3.2 p) | 3.5<br>(3.2 p) |
| **R = Et** | **Metal (%)** | 3.7<br>(1.8 s, 0.4 p, 1.4 d) | 10.7<br>(6.0 s, 1.5 p, 2.8 d) | 14.6<br>(8.9 s, 1.6 p, 2.6 d, 1.5 f) |
| | **Carbene (%)** | 43.8<br>(7.3 s, 35.9 p) | 35.4<br>(7.1 s, 28.0 p) | 38.5<br>(6.3 s, 31.8 p) |
| | **Nitrogen (%)** | 3.6<br>(3.5 p) | 3.2<br>(3.2 p) | 3.5<br>(3.3 p) |

**Table S9.** Composition analysis of the molecular orbitals (LUMO) of ($^{R}$CAAC)M($CH_2SiMe_3$)$_3$ (R = Me and Et, M = Sc, Y and Lu).

| **($^{R}$CAAC)M($CH_2SiMe_3$)$_3$** | | **Sc** | **Y** | **Lu** |
|---|---|---|---|---|
| **R = Me** | **Metal (%)** | 12.5<br>(2.1 p, 10.4 d) | 11.7<br>(2.5 p, 9.0 d) | 12.8<br>(2.5 p, 9.8 d, 0.4 f) |
| | **Carbene (%)** | 54.0<br>(53.0 p) | 54.3<br>(53.4 p) | 54.0<br>(53.1 p) |
| | **Nitrogen (%)** | 17.1<br>(16.1 p) | 17.3<br>(17.2 p) | 17.9<br>(17.3 p) |
| **R = Et** | **Metal (%)** | 12.8<br>(1.8 p, 11.0 d) | 9.4<br>(0.4 p, 8.7 d) | 12.3<br>(2.0 p, 9.9 d, 0.4 f) |
| | **Carbene (%)** | 53.9<br>(52.9 p) | 54.7<br>(53.7 p) | 54.5<br>(53.5 p) |
| | **Nitrogen (%)** | 16.9<br>(16.5 p) | 17.3<br>(17.2 p) | 17.7<br>(17.5 p) |

**Table S10.** Composition analysis of the molecular orbitals reflecting σ donation from the lone pair of the carbene to yttrium in ($^{Me}$CAAC)$_2$YI$_3$ (**3-Y**).

| | **HOMO-14** | **HOMO-12** |
|---|---|---|
| **Yttrium (%)** | 13.7<br>(13.1 s, 0.1 p, 0.2 d) | 16.7<br>(13.9 p, 2.6 d) |
| **Carbene (%)** | 21.8<br>(3.8 s, 17.4 p) | 36.1<br>(7.8 s, 27.8 p) |
| **Nitrogen (%)** | 8.1<br>(8.1 p) | 5.6<br>(5.2 p) |

**Table S11.** Composition analysis of LUMO and LUMO+1 for ($^{Me}$CAAC)$_2$YI$_3$ (**3-Y**).

| | **LUMO** | **LUMO+1** |
|---|---|---|
| **Yttrium (%)** | 27.7<br>(0.3 s, 27.4 d) | 12.6<br>(2.1 p, 10.1 d) |
| **Carbene (%)** | 40.8<br>(40.8 p) | 49.1<br>(48.7 p) |
| **Nitrogen (%)** | 13.1<br>(13.1 p) | 15.2<br>(15.2 p) |

**Table S12.** Summary for energy levels of the molecular orbitals reflecting the interaction between the rare-earth metal and the carbene in ($^{R}$CAAC)M(CH$_2$SiMe$_3$)$_3$ (R = Me and Et, M = Sc, Y and Lu) and ($^{Me}$CAAC)$_2$YI$_3$.

| | **($^{R}$CAAC)M(CH$_2$SiMe$_3$)$_3$** | | | | | | **($^{Me}$CAAC)$_2$YI$_3$** |
|---|---|---|---|---|---|---|---|
| | **R = Me** | | | **R = Et** | | | |
| | **M = Sc** | **M = Y** | **M = Lu** | **M = Sc** | **M = Y** | **M = Lu** | |
| **LUMO+1** | | | | | | | -1.28 |
| **LUMO** | -1.85 | -1.91 | -1.93 | -1.82 | -1.81 | -1.85 | -1.62 |
| **HOMO-12** | | | | | | | -7.44 |
| **HOMO-14** | -8.22 | -8.17 | -8.33 | -8.22 | -8.14 | -8.30 | -8.14 |

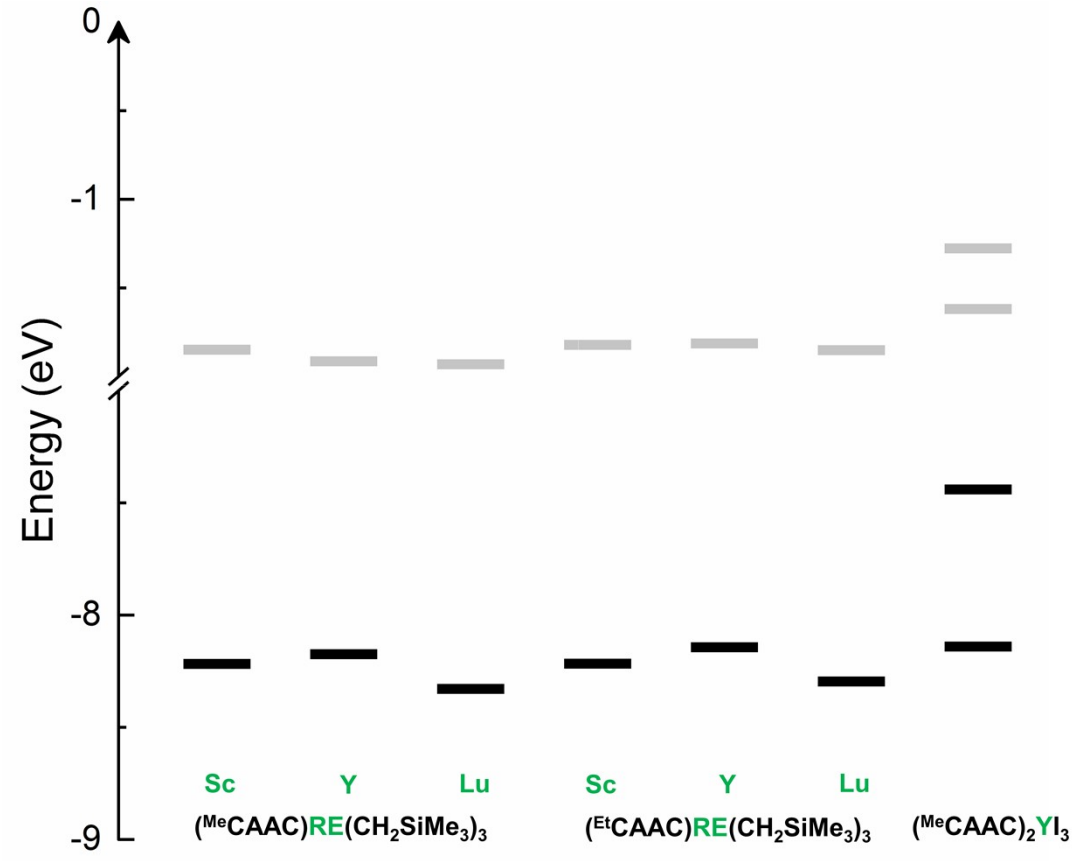



**Figure S39.** Energy level diagram of the molecular orbitals (LUMO, gray; HOMO-14, black) for ($^{R}$CAAC)M($CH_2SiMe_3$)$_3$ (R = Me and Et, M = Sc, Y and Lu); for $^{Me}$CAAC)$_2$YI$_3$, LUMO+1 (grey) and HOMO-12 (black) are shown as well.

**Table S13.** Cartesian coordinates for the optimized structure of ($^{Me}$CAAC)Sc($CH_2SiMe_3$)$_3$.

| | | | |
|---|---|---|---|
| Sc | 9.81292638523919 | 4.42107432103227 | 23.53306741575299 |
| Si | 7.37409011607802 | 1.77856038373616 | 24.09673082553619 |
| Si | 7.69122063096494 | 7.04855326328121 | 24.89438215804614 |
| Si | 8.75548132578757 | 4.51410490215584 | 19.97112711163795 |
| N | 13.21509890877355 | 4.39159729287052 | 23.89413021761449 |
| C | 13.32389400279111 | 4.16658169271128 | 22.46289848871885 |
| C | 12.05635576493943 | 4.41007558728716 | 24.51390771949021 |
| C | 9.74215914277635 | 3.81328410174919 | 21.40701483588043 |
| C | 13.34146945795929 | 2.82789018409321 | 21.98700259839815 |
| C | 7.89481890978760 | 6.66133219966791 | 26.75163720747420 |
| H | 8.00577251829182 | 5.57629064449866 | 26.93250680458653 |
| H | 7.00247604164323 | 7.00184637825602 | 27.30892525388800 |
| H | 8.77365190252170 | 7.17448551368381 | 27.18331029345269 |
| C | 13.35073738172820 | 5.27940392539912 | 21.58088930088934 |
| C | 13.16908521155461 | 6.72409178654990 | 22.03603504154776 |
| H | 13.11265636645564 | 6.73153946673071 | 23.13899107878576 |
| C | 6.23436978540599 | 1.11258479102377 | 25.47549443519200 |
| H | 6.82286047742520 | 0.61794651433549 | 26.27024305944278 |
| H | 5.50382664275556 | 0.38011856918116 | 25.08363380094022 |
| H | 5.66881662513642 | 1.93933525949973 | 25.94402769708276 |
| C | 13.44386828409091 | 2.62918122732931 | 20.59723241905601 |
| H | 13.44412688361149 | 1.60622368416078 | 20.20324879267864 |
| C | 14.46832267214704 | 4.54658450805980 | 24.77699938181833 |
| C | 12.31347521989133 | 4.54030176212764 | 26.00801233113684 |
| C | 9.18393379426851 | 6.52121839543276 | 23.88813370294358 |
| C | 13.16225773509946 | 1.61434942626426 | 22.89490913425937 |
| H | 13.28180115442345 | 1.94713696943428 | 23.93738419450057 |
| C | 11.37605764348661 | 5.56980992299857 | 26.65731205133001 |
| H | 11.59484124996927 | 5.65312846681099 | 27.73756627711196 |
| H | 10.31971880466931 | 5.27405330320422 | 26.54580524322007 |
| H | 11.49221272792996 | 6.56853800936665 | 26.20202517723189 |
| C | 13.80595785990901 | 4.95947013846719 | 26.10596684222102 |
| H | 13.86739391920224 | 6.05692495184278 | 26.22181816326705 |
| H | 14.31542586385204 | 4.50805901083227 | 26.97461213580216 |
| C | 7.96084985294565 | 3.11503434532512 | 18.94246705616089 |
| H | 8.73634914960149 | 2.42879025823616 | 18.55480008770513 |
| H | 7.39435341629721 | 3.51602033246866 | 18.08115850663842 |
| H | 7.26226210266860 | 2.51717124130665 | 19.55656045262609 |
| C | 8.62747072082505 | 3.00721763791784 | 24.76483810340839 |
| C | 6.11946142051763 | 6.15975681514475 | 24.29767521263870 |
| H | 5.95457445510413 | 6.32449221793568 | 23.21760546745496 |
| H | 5.22836254232759 | 6.52604121365523 | 24.83975772133341 |
| H | 6.19622472889235 | 5.07071163379487 | 24.46449756603868 |

| | | | |
|---|---|---|---|
| C | 11.83441743915345 | 7.28796220831348 | 21.51349953862628 |
| H | 11.87027321998986 | 7.42760184898229 | 20.41852897253379 |
| H | 11.61957714494943 | 8.26787753828606 | 21.97536337632708 |
| H | 10.98902173539597 | 6.61622131300810 | 21.73451407007186 |
| C | 13.45573607229368 | 5.01683131700760 | 20.20150750983911 |
| H | 13.45979871189282 | 5.85808225624027 | 19.49844721562161 |
| C | 13.51480607934639 | 3.70889535812614 | 19.71059894927716 |
| H | 13.58645921032746 | 3.53020177097542 | 18.63111088348148 |
| C | 14.21223838364099 | 0.52084937066767 | 22.63517841530522 |
| H | 14.11718307731960 | -0.28476656270024 | 23.38494390794589 |
| H | 15.24196925867606 | 0.91697432701570 | 22.68420603306891 |
| H | 14.08001675633214 | 0.05710388214986 | 21.64122814989849 |
| C | 15.24223652283943 | 3.22286581872334 | 24.86793241144361 |
| H | 14.65795812806326 | 2.42246486083161 | 25.34822821543830 |
| H | 16.14903792821676 | 3.38681175252658 | 25.47540142413419 |
| H | 15.56338856889889 | 2.87879383282549 | 23.87008501465550 |
| C | 12.05024300857854 | 3.15007973052329 | 26.63975956284807 |
| H | 12.26231634375926 | 3.19781076567797 | 27.72310863953070 |
| H | 12.68267476484891 | 2.36047036304563 | 26.19896858049218 |
| H | 10.99664160141351 | 2.85391282416232 | 26.50485948337448 |
| C | 15.40664975766062 | 5.62085343406558 | 24.22363468946483 |
| H | 15.76814712180830 | 5.35991808823553 | 23.21398982780357 |
| H | 16.28464397471086 | 5.70107119302135 | 24.88783810393366 |
| H | 14.92239359343298 | 6.60876529056692 | 24.18529309048677 |
| C | 7.37261455653421 | 8.92677336625650 | 24.75939542689936 |
| H | 8.24298621018002 | 9.50172135001130 | 25.12675296163217 |
| H | 6.48719021681247 | 9.23518283171375 | 25.34655973861184 |
| H | 7.20087161263473 | 9.21699170847979 | 23.70630535792223 |
| C | 9.87877069692674 | 5.50132758848278 | 18.78708711081783 |
| H | 10.26154087674948 | 6.42056571357227 | 19.26273588061928 |
| H | 9.31783057588020 | 5.79761152529465 | 17.88154039089887 |
| H | 10.74681221691226 | 4.89381812809154 | 18.47137997792992 |
| C | 14.33154325350382 | 7.63418027716091 | 21.59883638472357 |
| H | 15.31244292627123 | 7.26241130215974 | 21.93914138031625 |
| H | 14.19057291359744 | 8.65403244228540 | 21.99962896883333 |
| H | 14.37185450577656 | 7.71781733367679 | 20.49783189612360 |
| C | 11.73594133272008 | 1.04825419347680 | 22.78133493541426 |
| H | 11.48821641741495 | 0.77620425492606 | 21.73987407933320 |
| H | 10.97877882726795 | 1.77748815698638 | 23.11582556077222 |
| H | 11.62594164575664 | 0.14538143131859 | 23.40818908865284 |
| C | 8.26009573249862 | 0.28154452778356 | 23.31731994152574 |
| H | 8.82127704350947 | 0.57333262622520 | 22.41150800648530 |
| H | 7.52511704305639 | -0.49010318379184 | 23.02282680268808 |
| H | 8.97124991435012 | -0.18177862506989 | 24.02580855744259 |

| | | | |
|---|---|---|---|
| C | 7.34330945824255 | 5.67829818921876 | 20.50413919167566 |
| H | 6.64054542308383 | 5.17027181379363 | 21.18872628052318 |
| H | 6.76835860696947 | 6.02234427868837 | 19.62440733746303 |
| H | 7.73299736450447 | 6.57057362237239 | 21.02716592023568 |
| C | 6.25127732812493 | 2.52325899670821 | 22.75247199697789 |
| H | 5.64057791887318 | 3.35933026459439 | 23.13705511043872 |
| H | 5.56004044920843 | 1.75396063713143 | 22.36117122914026 |
| H | 6.84856023782805 | 2.90411467191353 | 21.90601243700076 |
| H | 9.35795920012895 | 2.78261917245435 | 21.59176377186764 |
| H | 10.79150884909790 | 3.68414126950551 | 21.06379589080509 |
| H | 9.01243738038987 | 6.88847811174171 | 22.85056563997363 |
| H | 10.07492652109548 | 7.07599895056331 | 24.26203560019009 |
| H | 9.32105726777846 | 2.42490058384336 | 25.41257575821378 |
| H | 8.09569727302457 | 3.71438765629253 | 25.44296395730619 |

**Table S14.** Cartesian coordinates for the optimized structure of ($^{Et}$CAAC)Sc($CH_2SiMe_3$)$_3$.

| | | | |
|---|---|---|---|
| Sc | 11.44671018627043 | 4.28699537371783 | 14.65385819138304 |
| Si | 12.81366176427446 | 5.10765996959711 | 17.85520230516212 |
| Si | 13.85032594702975 | 1.66598186705272 | 13.76453255681958 |
| Si | 12.81946158545905 | 7.31493247976090 | 12.91154183932111 |
| N | 8.02429632706939 | 3.96390206306919 | 14.40177241212011 |
| C | 9.18817189016204 | 3.91505105107663 | 13.79898596459201 |
| C | 7.86813889034388 | 4.41686021414072 | 15.77419525867320 |
| C | 7.96653124984970 | 3.48990462584564 | 16.84469799586596 |
| C | 6.80320915097787 | 3.53546343548751 | 13.56891857107797 |
| C | 8.38470093094228 | 2.03385735109389 | 16.67056476553407 |
| H | 8.46661309758644 | 1.82723451001433 | 15.58995262913597 |
| C | 7.66386699355065 | 5.80504705448843 | 15.99997067164800 |
| C | 8.98075755393088 | 3.56142077958095 | 12.34114837700009 |
| C | 7.78045122228540 | 3.97987763922283 | 18.15240328246658 |
| H | 7.86098274181898 | 3.28393924356179 | 18.99602050950558 |
| C | 7.49461951391612 | 6.23588781739067 | 17.32880621901520 |
| H | 7.34921442427425 | 7.30407610445780 | 17.52828955300058 |
| C | 7.71265276143720 | 6.85207408473566 | 14.89064730610410 |
| H | 7.70384103847934 | 6.32693002546172 | 13.92113817052764 |
| C | 9.78258281159195 | 1.81601849912614 | 17.28039099553943 |
| H | 10.51377468504853 | 2.54907373772132 | 16.90265689712842 |
| H | 10.16012965908450 | 0.80583967799751 | 17.04165104075335 |
| H | 9.75631330557939 | 1.91924374514479 | 18.38002890721986 |
| C | 9.44028875989604 | 4.83153877669184 | 11.55848446864904 |
| H | 8.80832378581576 | 5.68034200094288 | 11.88730926806224 |
| H | 10.46870548627149 | 5.09106493451548 | 11.87311697545132 |
| C | 7.53335364591773 | 5.33383650543502 | 18.39714021764513 |
| H | 7.40014852484023 | 5.69210654006750 | 19.42493273146480 |
| C | 7.37632770751178 | 1.04094698991086 | 17.27454174465822 |
| H | 7.30761708039640 | 1.16056168189805 | 18.37089542576535 |
| H | 7.69880635058558 | 0.00279629676293 | 17.07770067614935 |
| H | 6.36105967259777 | 1.16819511290201 | 16.86184747545971 |
| C | 12.41675469578944 | 2.29558959909125 | 14.79717119623506 |
| C | 7.45119997874802 | 3.31696920712492 | 12.18063099284393 |
| H | 7.02102321169469 | 4.01864726048574 | 11.44527685824144 |
| H | 7.23655919931427 | 2.30057396681993 | 11.81059628662218 |
| C | 9.85805300025556 | 2.34403933621348 | 11.95998665564551 |
| H | 9.75911649443200 | 2.16954324177578 | 10.87238499435436 |
| H | 10.91687785338797 | 2.61762389910890 | 12.12852021841752 |
| C | 14.49122194389962 | 5.22630121800282 | 16.96229580713507 |
| H | 14.61260610397492 | 4.40814324978933 | 16.23044206421368 |
| H | 15.33316475699230 | 5.16902304702491 | 17.67661152706979 |
| H | 14.57901351129959 | 6.18205371978342 | 16.41311315781485 |

| | | | |
|---|---|---|---|
| C | 11.41338828179213 | 5.28834217422016 | 16.62499588817397 |
| C | 9.03386548210688 | 7.63868431903665 | 14.94738989436427 |
| H | 9.16866328591429 | 8.12994056270470 | 15.92779394957337 |
| H | 9.05497245894854 | 8.41882621195189 | 14.16578956361875 |
| H | 9.90238884635398 | 6.97784864319948 | 14.79099379657100 |
| C | 6.21440529174044 | 2.24692619099021 | 14.15418614300456 |
| H | 6.94945786446186 | 1.42603594418818 | 14.16196770663112 |
| H | 5.35738524958146 | 1.93323683481904 | 13.53320638724873 |
| H | 5.84708197090222 | 2.40763418171063 | 15.18161926789043 |
| C | 5.71625490921850 | 4.61561970849701 | 13.55858974121268 |
| H | 5.38364836992221 | 4.86436995430129 | 14.58127794098991 |
| H | 4.84326209134147 | 4.23063231697114 | 13.00352035632307 |
| H | 6.05040222754837 | 5.53813990114393 | 13.05818364563497 |
| C | 6.50465512660875 | 7.80424230507649 | 14.91903761404827 |
| H | 5.54631623765721 | 7.25663880295977 | 14.90867113600214 |
| H | 6.52818312552996 | 8.47586407657655 | 14.04220665903660 |
| H | 6.51448051083193 | 8.44424836555209 | 15.81942917639069 |
| C | 12.77740046928355 | 6.47878301613834 | 19.18389952629615 |
| H | 13.60840348162061 | 6.37371699022532 | 19.90659832251173 |
| H | 11.82669798097789 | 6.45283973638818 | 19.74824660959168 |
| H | 12.85946822045947 | 7.47578874460730 | 18.71239161103274 |
| C | 9.54906070565259 | 1.04846187127445 | 12.71188074190770 |
| H | 10.27008204563091 | 0.25943829761166 | 12.43603466530675 |
| H | 8.53845148986746 | 0.66358643202014 | 12.48397558816808 |
| H | 9.62396768050374 | 1.18478655758394 | 13.80582997044995 |
| C | 12.74215784604804 | 3.43937791073056 | 18.77359529478072 |
| H | 12.83160807346743 | 2.58486032746953 | 18.07856011526525 |
| H | 11.78882580121642 | 3.33155486517382 | 19.32287962796637 |
| H | 13.56550745475344 | 3.36585758918234 | 19.50786316213772 |
| C | 13.51657279294615 | 1.77038253949557 | 11.88749954922465 |
| H | 13.32184927283559 | 2.81050562466026 | 11.56816154755128 |
| H | 12.65501396719361 | 1.14648985605269 | 11.58623613792763 |
| H | 14.39820210354715 | 1.40708520163448 | 11.32736588222940 |
| C | 9.38473446575415 | 4.71873832254183 | 10.03366263688795 |
| H | 9.63413672153678 | 5.69295077872027 | 9.57802255164352 |
| H | 8.38096736652651 | 4.42947939704201 | 9.67063891693620 |
| H | 10.10949878587132 | 3.98132595100757 | 9.64774210989540 |
| C | 15.44363899962064 | 2.64539245245641 | 14.11165902330526 |
| H | 15.72176025716406 | 2.59093837912586 | 15.18001655277928 |
| H | 15.33346819401794 | 3.71118725542810 | 13.84218211487496 |
| H | 16.28459983860786 | 2.23307564182795 | 13.52397911700363 |
| C | 12.81953883967038 | 8.36211805167514 | 14.50284205770302 |
| H | 11.86167900170778 | 8.29876471110029 | 15.04795691117569 |
| H | 13.00886453892723 | 9.42611643721684 | 14.26939829039833 |

| | | | |
|---|---|---|---|
| H | 13.61515029761382 | 8.02078463954298 | 15.19038001505829 |
| C | 14.22401165695667 | -0.17090951839270 | 14.13589218411817 |
| H | 15.07279778869953 | -0.54747998693730 | 13.53447571615947 |
| H | 13.34364142728836 | -0.80308556664490 | 13.91442445359328 |
| H | 14.47359705646417 | -0.31044074796477 | 15.20398704837065 |
| C | 14.42410383422121 | 7.74730222841085 | 11.97245477548213 |
| H | 15.31111836079326 | 7.47829946417083 | 12.57540983563986 |
| H | 14.48584651733913 | 8.82661010768381 | 11.73740676214689 |
| H | 14.48586614106670 | 7.18588225293445 | 11.02182152393052 |
| H | 11.59562034814570 | 1.54668174595449 | 14.73132425849105 |
| H | 10.44167407758970 | 5.13100849850482 | 17.14095467801291 |
| H | 12.75044546653102 | 2.27575289484177 | 15.86005348842719 |
| H | 11.42776430714750 | 6.35464964698576 | 16.30275997152660 |
| C | 12.70849821006017 | 5.48544140722704 | 13.28674247579494 |
| H | 12.77607828485610 | 4.92664223390203 | 12.32569882102396 |
| H | 13.64772391723405 | 5.22383851547580 | 13.83306689124312 |
| C | 11.37385495009273 | 7.88934323650804 | 11.80417113987483 |
| H | 11.36894092475913 | 7.33888789139160 | 10.84489800502863 |
| H | 10.39639817452803 | 7.73113450146001 | 12.29234660723221 |
| H | 11.46807103815843 | 8.96605518856124 | 11.57078068568409 |

**Table S15.** Cartesian coordinates for the optimized structure of ($^{Me}$CAAC)Y($CH_2SiMe_3$)$_3$.

| | | | |
|---|---|---|---|
| Y | 1.65485746629395 | 12.03954987495587 | 13.75588733906421 |
| Si | 2.80708548392673 | 14.75074322083626 | 15.94824731007338 |
| Si | 0.19256940938927 | 14.21739571129308 | 11.04845061141014 |
| Si | 5.02400698453328 | 10.88565902564028 | 12.38508149064115 |
| N | -0.09810870272589 | 9.33202167832284 | 15.29879221413300 |
| C | 0.33358331658354 | 9.86293373962990 | 14.17952377290378 |
| C | -0.13911827477293 | 9.00985269821552 | 13.01721513520102 |
| C | -1.19435518865924 | 8.05227675131159 | 13.63699036477293 |
| H | -1.12794627732019 | 7.03054713217970 | 13.22527847202720 |
| H | -2.20820339114391 | 8.43073676113792 | 13.41367887839816 |
| C | -0.96438727786331 | 8.06578151342304 | 15.16325118791445 |
| C | 1.10496998746670 | 8.26762054410467 | 12.47153163099192 |
| H | 1.87273403996886 | 8.98285965930091 | 12.12876382325325 |
| H | 0.81072956533953 | 7.63822764334438 | 11.61216576540662 |
| H | 1.57095997764526 | 7.61765434108223 | 13.23206475860674 |
| C | -0.73427718859585 | 9.88934810989885 | 11.90316741510820 |
| H | -1.57421579838162 | 10.50267885344106 | 12.27484534922416 |
| H | -1.10858509061840 | 9.25507486158608 | 11.07897354650574 |
| H | 0.02004099021487 | 10.57453911614482 | 11.47806500951095 |
| C | -0.20204886431027 | 6.83509712471094 | 15.67094788171841 |
| H | 0.71742244961127 | 6.64124964599993 | 15.09569278414026 |
| H | -0.85413901553195 | 5.94985032504175 | 15.57416872155792 |
| H | 0.06247392389004 | 6.94371906649130 | 16.73596926734355 |
| C | -2.26435435604384 | 8.20712473868015 | 15.95864798066146 |
| H | -2.06611115041556 | 8.33902382681493 | 17.03651788869393 |
| H | -2.86083766866114 | 7.28677375665378 | 15.83297555219535 |
| H | -2.87196312727856 | 9.05407024616324 | 15.60308855594598 |
| C | 0.22360927343539 | 9.88200147561407 | 16.60520829785002 |
| C | -0.63497795208221 | 10.86499256586583 | 17.16684138096056 |
| C | -0.32335619803649 | 11.35120971202037 | 18.45073164325664 |
| H | -0.96683493799335 | 12.11704893370561 | 18.89977437254821 |
| C | 0.80194954975303 | 10.90069275627102 | 19.14772083215517 |
| H | 1.02660555929428 | 11.29640318565720 | 20.14533821750193 |
| C | 1.66200970930713 | 9.97468228571303 | 18.55000478491034 |
| H | 2.57231093766601 | 9.66537420976600 | 19.07704691200917 |
| C | 1.40347620540454 | 9.45090615733462 | 17.26881011170552 |
| C | -1.79807218267470 | 11.50301981091168 | 16.41309092154241 |
| H | -1.91970826483586 | 10.97440565586004 | 15.45037228278924 |
| C | -1.46316264388282 | 12.97059448756541 | 16.08544527440501 |
| H | -1.40176639350371 | 13.57916660338709 | 17.00537473285417 |
| H | -2.23412362677108 | 13.41387844568797 | 15.43082332802136 |
| H | -0.49186102788717 | 13.06837015310323 | 15.57347693632163 |
| C | -3.12928597742187 | 11.41514405377143 | 17.18071825899528 |

| | | | |
|---|---|---|---|
| H | -3.39029785858564 | 10.37741327287750 | 17.44913617861030 |
| H | -3.95069999750761 | 11.83170310853018 | 16.57058959049822 |
| H | -3.08880105645550 | 12.00057315297004 | 18.11684784631159 |
| C | 2.45337442228892 | 8.54647623445121 | 16.62992936377386 |
| H | 2.04794801664322 | 8.16061515068325 | 15.68009107559230 |
| C | 3.70952559359823 | 9.36347710515332 | 16.27664260711444 |
| H | 3.47078838450281 | 10.18569680666772 | 15.58191050735082 |
| H | 4.47248397231416 | 8.72328164920370 | 15.80032179012696 |
| H | 4.15684478273300 | 9.82289490793428 | 17.17631430588843 |
| C | 2.82113271423979 | 7.34046997221385 | 17.51186991235875 |
| H | 3.33038764195034 | 7.65989439745461 | 18.43876021350758 |
| H | 3.51431530652622 | 6.67071318894978 | 16.97231436333380 |
| H | 1.93460524666991 | 6.75205338270097 | 17.80583289338647 |
| C | 2.52434167781516 | 12.90830398786867 | 15.79530059092414 |
| H | 1.92298847476858 | 12.54566612887064 | 16.65836444826990 |
| H | 3.52622125174352 | 12.43187675986612 | 15.89448605396928 |
| C | 3.92676285453831 | 15.22186860287638 | 17.42176127461518 |
| H | 3.47812549023180 | 14.88741068430569 | 18.37562508714051 |
| H | 4.08771819407782 | 16.31473820561052 | 17.48331430884414 |
| H | 4.91585922844162 | 14.73617208754334 | 17.32878885885822 |
| C | 1.16615070565034 | 15.69498043093668 | 16.17240257865690 |
| H | 0.48660523899474 | 15.53537117429686 | 15.31586682685879 |
| H | 1.34751585686278 | 16.78181939631979 | 16.26318701381100 |
| H | 0.64233099289337 | 15.36268822153401 | 17.08785976845275 |
| C | 3.65493624593380 | 15.38508284769703 | 14.36251774299340 |
| H | 4.59958095868207 | 14.83897296818047 | 14.18031230091247 |
| H | 3.89493611356305 | 16.46239185789939 | 14.42723949391220 |
| H | 3.00890850599454 | 15.24136378989888 | 13.47694315468846 |
| C | 0.07232691660880 | 13.52919088669541 | 12.78712303643692 |
| H | -0.89566831381969 | 12.97959910477396 | 12.87855242916222 |
| H | -0.00903377930015 | 14.39686681894764 | 13.48035014406116 |
| C | 1.72953764829600 | 15.32552636404493 | 10.86369170713108 |
| H | 1.71052792653157 | 16.15635696038285 | 11.59270573963544 |
| H | 1.77463302764984 | 15.76696891527927 | 9.85101407866894 |
| H | 2.66187814173040 | 14.75452906251097 | 11.02456865913021 |
| C | -1.32290416640915 | 15.27882120722625 | 10.57111091175459 |
| H | -2.25351615486858 | 14.68352790381963 | 10.62463993762164 |
| H | -1.23410208458054 | 15.67989844319987 | 9.54378417311397 |
| H | -1.43371991161264 | 16.13447092312733 | 11.26270571133016 |
| C | 0.31574769565934 | 12.82974728326590 | 9.74402700258792 |
| H | 1.20359612058939 | 12.19433194127019 | 9.91763725637889 |
| H | 0.40372047375484 | 13.26033019035736 | 8.72934272580313 |
| H | -0.58297137471532 | 12.18546310463505 | 9.75342612115674 |
| C | 3.33217650117743 | 11.63132989934947 | 12.11386583153384 |

| | | | |
|---|---|---|---|
| H | 2.85308368265496 | 11.09866295817132 | 11.26006308996324 |
| H | 3.47825990641155 | 12.67748058584024 | 11.75270282689773 |
| C | 6.20664726618970 | 11.13419596249587 | 10.90744338036546 |
| H | 5.78016467508825 | 10.69821741388141 | 9.98517868752971 |
| H | 7.19188840721257 | 10.66338108798830 | 11.08568750975470 |
| H | 6.37333603987346 | 12.21117595913558 | 10.72023229672569 |
| C | 5.88568154471383 | 11.65374481338309 | 13.90234254652194 |
| H | 5.94717751831258 | 12.75245454339004 | 13.79158009324731 |
| H | 6.91591669637436 | 11.26797862092396 | 14.01326165198189 |
| H | 5.34129602188178 | 11.44832758658591 | 14.84086664686408 |
| C | 4.87233467399472 | 8.99860041390903 | 12.64757873694457 |
| H | 4.17782695399646 | 8.75558493160779 | 13.47112952338632 |
| H | 5.85398719015840 | 8.54877241916943 | 12.88568392270963 |
| H | 4.49398754502452 | 8.50869376249592 | 11.73081247560755 |

**Table S16.** Cartesian coordinates for the optimized structure of ($^{Et}$CAAC)Y($CH_2SiMe_3$)$_3$.

| | | | |
|---|---|---|---|
| Y | 11.59543501088020 | 4.59662845191339 | 8.20348434257774 |
| Si | 12.93262370985343 | 5.01468450618354 | 4.89964337293502 |
| Si | 14.11275406392220 | 1.60670810431756 | 9.11039280885238 |
| Si | 13.69752117280464 | 6.56434797983445 | 10.64911187305511 |
| N | 8.13537056529537 | 3.88120255581125 | 8.64965536981667 |
| C | 9.31382223458698 | 3.94549308474924 | 9.21979743399245 |
| C | 9.17751971197567 | 3.62024693083298 | 10.69294290882630 |
| C | 7.68555531761689 | 3.22221822753906 | 10.89500532603804 |
| H | 7.58980646326694 | 2.17445582568276 | 11.22427006469624 |
| H | 7.21250615895423 | 3.84376177500849 | 11.67425380539914 |
| C | 6.96795411420508 | 3.42336299438538 | 9.53796554432160 |
| C | 5.87242676047194 | 4.49301258980468 | 9.59882572689225 |
| H | 6.23308951612922 | 5.42701335790436 | 10.05876261322968 |
| H | 5.03949476989126 | 4.11279464203694 | 10.21527184597050 |
| H | 5.47449371828515 | 4.71983325207509 | 8.59474644284213 |
| C | 6.37146474437126 | 2.12404247669860 | 8.98889020021762 |
| H | 5.95140838778237 | 2.27156219872043 | 7.97956542346248 |
| H | 5.55132972984088 | 1.79980573665015 | 9.65288057558110 |
| H | 7.11955732007616 | 1.31551104418568 | 8.95135180880643 |
| C | 9.52169925940990 | 4.95222780956190 | 11.43248043061374 |
| H | 10.52171169741783 | 5.29572366630211 | 11.10554909894004 |
| H | 8.81139086809283 | 5.72877142596143 | 11.08463707069972 |
| C | 9.49181407608724 | 4.87799310712674 | 12.96056680909835 |
| H | 8.53032297642509 | 4.48893318373713 | 13.34368545058222 |
| H | 9.63565463400448 | 5.88502530931381 | 13.38929637041012 |
| H | 10.30104117803700 | 4.24089478913586 | 13.35620307473649 |
| C | 10.18285993509000 | 2.50744135048899 | 11.08577536387800 |
| H | 11.20503395014676 | 2.86920607850330 | 10.85746910936999 |
| H | 10.14838133714262 | 2.37467582579336 | 12.18305654501293 |
| C | 9.96747017541745 | 1.15416774683873 | 10.40472371384471 |
| H | 9.94290850528740 | 1.24786708581292 | 9.30390311158078 |
| H | 9.02774704400031 | 0.66875472254162 | 10.72459155338222 |
| H | 10.79308784910739 | 0.46338514678775 | 10.64867728737361 |
| C | 7.92176676370189 | 4.25640205534659 | 7.26055613435484 |
| C | 7.64228685670103 | 5.61797817579093 | 6.96063997457321 |
| C | 7.39880255344420 | 5.95574154436744 | 5.61607172183877 |
| H | 7.18965780383289 | 7.00087652965830 | 5.35900098648053 |
| C | 7.44303050350131 | 4.99317966957615 | 4.60276294698105 |
| H | 7.24980825660681 | 5.28032376044476 | 3.56233403485172 |
| C | 7.77820683833525 | 3.67246482337114 | 4.91572750854047 |
| H | 7.86928697569679 | 2.93276291206241 | 4.11138004928932 |
| C | 8.03921980044584 | 3.27398032147493 | 6.24103219794782 |
| C | 8.55326754753409 | 1.85834239466098 | 6.48370944799068 |

| | | | |
|---|---|---|---|
| H | 8.67992891558631 | 1.72119761971427 | 7.57136785026225 |
| C | 7.59257892436836 | 0.77105039415428 | 5.97155745796497 |
| H | 6.58239518707148 | 0.86425119441365 | 6.40490963972086 |
| H | 7.98273625943746 | -0.23156121187950 | 6.22263614199758 |
| H | 7.48972265723143 | 0.81613391407806 | 4.87234389301863 |
| C | 9.94430210364574 | 1.68795010782445 | 5.8416650777919 |
| H | 9.88007729077706 | 1.72212063114881 | 4.73910238675475 |
| H | 10.39146070708365 | 0.71959263247992 | 6.12871406921625 |
| H | 10.64065101562000 | 2.48610757182975 | 6.14587939295440 |
| C | 7.68614702943509 | 6.73858591158340 | 7.99670304079801 |
| H | 7.79242751853617 | 6.28216665633932 | 8.99552895674382 |
| C | 6.40719517914121 | 7.59475213257492 | 8.00134578631845 |
| H | 6.29855763523406 | 8.15988501690818 | 7.05825484807784 |
| H | 6.44551853644715 | 8.33392838653725 | 8.82156580130192 |
| H | 5.49700235001184 | 6.98459053992577 | 8.13076470888530 |
| C | 8.92638833989944 | 7.62621458890326 | 7.78140811261059 |
| H | 9.86331115456808 | 7.04747195537524 | 7.83812513816379 |
| H | 8.97327248811224 | 8.41738574966285 | 8.55111873998302 |
| H | 8.90334775807272 | 8.11185264720778 | 6.78933938899668 |
| C | 11.39562843313238 | 5.27891953788450 | 5.93558354557645 |
| H | 10.50093081704421 | 4.87688880361301 | 5.41567156231928 |
| H | 11.24031732550209 | 6.37885712143081 | 6.02105067343687 |
| C | 12.98476171986065 | 3.25638766399458 | 4.16572895324570 |
| H | 13.00775357771506 | 2.48336963845400 | 4.95489193049851 |
| H | 13.88386490709730 | 3.12112653670257 | 3.53676254524727 |
| H | 12.09733990151192 | 3.06890713972250 | 3.53311565395149 |
| C | 13.08495297404679 | 6.23959213166397 | 3.44364675104444 |
| H | 12.22564435269628 | 6.13653136521571 | 2.75542877808494 |
| H | 14.01199134126390 | 6.07361002202761 | 2.86311445399890 |
| H | 13.09595804702558 | 7.28248939264197 | 3.81125672096713 |
| C | 14.47673596629568 | 5.24940029989754 | 6.00020953589474 |
| H | 14.47355222632850 | 6.24584896561700 | 6.48124752869081 |
| H | 15.41141783592410 | 5.16451030810726 | 5.41552961039391 |
| H | 14.52361367006024 | 4.48698926365726 | 6.80122748786069 |
| C | 12.73338497660191 | 2.51381047123358 | 8.23061684610212 |
| H | 11.80348148964972 | 1.91467106217224 | 8.39469591026910 |
| H | 12.94149630274686 | 2.40640581004404 | 7.13998922099683 |
| C | 13.93061567609278 | -0.28850816552795 | 8.92640833296055 |
| H | 12.97289720435727 | -0.63685641795444 | 9.35769260398914 |
| H | 14.74810589388118 | -0.83245226843726 | 9.43623053204054 |
| H | 13.93996303371633 | -0.57975347710068 | 7.85965280810692 |
| C | 14.14145256124784 | 1.95187862442733 | 10.98636575463616 |
| H | 14.30298563127256 | 3.02235050847527 | 11.20218403668444 |
| H | 14.95326408857156 | 1.38151706890100 | 11.47488876077923 |

| | | | |
|---|---|---|---|
| H | 13.19143454522354 | 1.64859007131564 | 11.46529046538711 |
| C | 15.80240318439497 | 2.07593827635208 | 8.37067761290736 |
| H | 15.81744880803454 | 1.86876863301157 | 7.28459380343935 |
| H | 16.61269860991969 | 1.48764026974219 | 8.83938880635189 |
| H | 16.03668074013893 | 3.14570059470691 | 8.51192589986524 |
| C | 12.33773528907522 | 6.55069243951871 | 9.36723141067387 |
| H | 12.67623455842110 | 7.18377398220055 | 8.51232294816431 |
| H | 11.44515961673225 | 7.07050368879456 | 9.78504832413195 |
| C | 14.22335319528239 | 8.31574056487543 | 11.19994881096596 |
| H | 14.58966634669611 | 8.90212698204329 | 10.33707196643455 |
| H | 15.03138030433258 | 8.28117777484354 | 11.95508696721839 |
| H | 13.36961230489026 | 8.86501559866629 | 11.63868011662160 |
| C | 13.14239017543344 | 5.65025689394719 | 12.23240201535892 |
| H | 12.30387059637838 | 6.18228838265270 | 12.71926937808483 |
| H | 13.96930774858827 | 5.59542374824157 | 12.96442369632621 |
| H | 12.81485878023781 | 4.61592346402000 | 12.02205723942713 |
| C | 15.24107075468799 | 5.69920641600869 | 9.95147304005633 |
| H | 14.99556025213195 | 4.67512001927643 | 9.62060285689081 |
| H | 16.05247440036284 | 5.63377953013360 | 10.69922950490105 |
| H | 15.63013792943707 | 6.24535965500983 | 9.07230668757002 |

**Table S17.** Cartesian coordinates for the optimized structure of ($^{Me}$CAAC)Lu($CH_2SiMe_3$)$_3$.

| | | | |
|---|---|---|---|
| Lu | 1.02374897 | 4.71539907 | 29.05278588 |
| Si | 3.43208159 | 7.42448132 | 28.16956106 |
| Si | 2.30163419 | 4.09674913 | 32.42143323 |
| Si | 2.37238848 | 1.59095446 | 27.39261065 |
| N | -2.44495705 | 5.01274863 | 28.64290236 |
| C | -1.27037671 | 5.03756855 | 28.07394379 |
| C | -1.44300290 | 5.40588971 | 26.61475391 |
| C | -2.90633508 | 5.89851939 | 26.50075900 |
| H | -2.92234117 | 6.99792067 | 26.48174893 |
| H | -3.39132527 | 5.54553980 | 25.58094734 |
| C | -3.64338845 | 5.39390356 | 27.75185618 |
| C | -1.17847239 | 4.12308344 | 25.79835917 |
| H | -0.16135312 | 3.74818626 | 25.97410964 |
| H | -1.28394884 | 4.34660311 | 24.72640267 |
| H | -1.88079445 | 3.31731435 | 26.05293586 |
| C | -0.43679483 | 6.48345860 | 26.19366958 |
| H | -0.54307697 | 7.39367931 | 26.80043833 |
| H | -0.59759350 | 6.75233513 | 25.13890450 |
| H | 0.59937396 | 6.13086583 | 26.29232997 |
| C | -4.52555846 | 4.17495947 | 27.48251931 |
| H | -3.99307034 | 3.37830266 | 26.94947272 |
| H | -5.37418753 | 4.48967776 | 26.85957300 |
| H | -4.93003830 | 3.76681748 | 28.41754862 |
| C | -4.48925848 | 6.47640088 | 28.41369944 |
| H | -4.91605149 | 6.12849936 | 29.36433026 |
| H | -5.32127554 | 6.73043407 | 27.74227263 |
| H | -3.91099369 | 7.38947976 | 28.59581535 |
| C | -2.64389350 | 4.62277439 | 30.03001210 |
| C | -2.60369254 | 5.61516707 | 31.03431610 |
| C | -2.84193419 | 5.21354296 | 32.35429076 |
| H | -2.80666634 | 5.96057425 | 33.14834415 |
| C | -3.08975979 | 3.88386780 | 32.67472219 |
| H | -3.26738171 | 3.59437784 | 33.71149984 |
| C | -3.06850397 | 2.91862372 | 31.67488750 |
| H | -3.21066460 | 1.86978780 | 31.93815333 |
| C | -2.83891116 | 3.25762609 | 30.33601217 |
| C | -2.20753895 | 7.06203955 | 30.78386466 |
| H | -2.08485656 | 7.20804996 | 29.70116415 |
| C | -3.25623486 | 8.06187138 | 31.29108361 |
| H | -4.25043925 | 7.87727485 | 30.86387564 |
| H | -2.95479099 | 9.08776872 | 31.03440277 |
| H | -3.34921350 | 8.01262068 | 32.38552987 |
| C | -0.84802165 | 7.35045320 | 31.43961268 |

| | | | |
|---|---|---|---|
| H | -0.92311432 | 7.29719879 | 32.53532923 |
| H | -0.49403681 | 8.35530891 | 31.16921165 |
| H | -0.08113894 | 6.62888485 | 31.13142034 |
| C | -2.71673296 | 2.13290993 | 29.31867310 |
| H | -2.63398163 | 2.57604469 | 28.31801052 |
| C | -3.93068624 | 1.19360593 | 29.32399314 |
| H | -3.99871270 | 0.63607443 | 30.26901965 |
| H | -3.83832423 | 0.45504609 | 28.51476145 |
| H | -4.87675359 | 1.73502618 | 29.18812244 |
| C | -1.42870836 | 1.33330738 | 29.56229160 |
| H | -0.53779533 | 1.96774114 | 29.47123311 |
| H | -1.34156935 | 0.51412817 | 28.83481804 |
| H | -1.41651226 | 0.89935082 | 30.57249565 |
| C | 1.91796703 | 6.85379941 | 29.08647215 |
| H | 1.06167015 | 7.49090730 | 28.77246468 |
| H | 2.07701592 | 7.08591053 | 30.15889414 |
| C | 3.76437024 | 9.27977076 | 28.39234540 |
| H | 2.91569316 | 9.87713697 | 28.02455284 |
| H | 4.66558151 | 9.60373988 | 27.84831186 |
| H | 3.90561576 | 9.52526024 | 29.45606283 |
| C | 3.27909834 | 7.12458277 | 26.30407690 |
| H | 3.13549309 | 6.05701264 | 26.07880383 |
| H | 4.19199007 | 7.45445198 | 25.78482912 |
| H | 2.43548124 | 7.68507956 | 25.87264063 |
| C | 4.96772869 | 6.50661325 | 28.78222163 |
| H | 5.10269538 | 6.63656936 | 29.86679470 |
| H | 5.87399380 | 6.88565705 | 28.28564338 |
| H | 4.90257208 | 5.42734778 | 28.57913996 |
| C | 0.95087396 | 3.80037086 | 31.18133085 |
| H | -0.03211118 | 4.00757680 | 31.64845578 |
| H | 0.96209147 | 2.71045933 | 30.97095290 |
| C | 2.23812255 | 5.85930130 | 33.11245179 |
| H | 2.34726846 | 6.61499842 | 32.32066960 |
| H | 3.04513304 | 6.02067574 | 33.84341543 |
| H | 1.28227127 | 6.04625637 | 33.62569648 |
| C | 2.21109821 | 2.92280537 | 33.90930129 |
| H | 1.25558345 | 3.04204349 | 34.44308117 |
| H | 3.02569993 | 3.10489513 | 34.62792483 |
| H | 2.27878100 | 1.87449051 | 33.58019641 |
| C | 3.98397372 | 3.82880964 | 31.59698358 |
| H | 4.04516491 | 2.81884862 | 31.16301806 |
| H | 4.81024478 | 3.93444931 | 32.31639762 |
| H | 4.15718593 | 4.55057434 | 30.78490814 |
| C | 2.32428148 | 3.43150785 | 27.62620065 |

| | | | |
|---|---|---|---|
| H | 2.26019238 | 3.90772728 | 26.62526696 |
| H | 3.31901708 | 3.73794224 | 28.02006400 |
| C | 3.86769043 | 1.00481006 | 26.38499110 |
| H | 3.87682422 | 1.47208188 | 25.38841812 |
| H | 3.86819125 | -0.08801173 | 26.24746396 |
| H | 4.80681101 | 1.28160897 | 26.88802835 |
| C | 0.83066561 | 0.99916554 | 26.45578744 |
| H | -0.09801005 | 1.30920575 | 26.95594727 |
| H | 0.81911471 | -0.09853048 | 26.37335660 |
| H | 0.81402701 | 1.40629915 | 25.43280775 |
| C | 2.45460390 | 0.68711929 | 29.05409221 |
| H | 3.33750719 | 1.01102384 | 29.62629092 |
| H | 2.53562339 | -0.40067929 | 28.90582942 |
| H | 1.57045024 | 0.87765135 | 29.67900938 |

**Table S18.** Cartesian coordinates for the optimized structure of ($^{Et}$CAAC)Lu($CH_2SiMe_3$)$_3$.

| | | | |
|---|---|---|---|
| Lu | 9.81774310316797 | 4.21313476160780 | 14.76136604043809 |
| Si | 8.47760668936601 | 4.99198200343752 | 18.05263486461937 |
| Si | 7.27729739427017 | 1.63194605979510 | 13.84508044469906 |
| Si | 8.53851542474330 | 7.32539927367675 | 12.94743667515518 |
| N | 13.30371423929856 | 3.90998946003091 | 14.43742517523352 |
| C | 12.31846006059045 | 3.39883935493237 | 12.41505897693190 |
| C | 13.46481855697327 | 4.36548332827026 | 15.80946119640965 |
| C | 12.99012247079985 | 1.96197349091835 | 16.67248647357507 |
| H | 12.93147928008219 | 1.76243268612555 | 15.58930479367828 |
| C | 11.42530131225912 | 2.17717140050125 | 12.08685762933851 |
| H | 10.36582181893315 | 2.47941530634382 | 12.19772089521569 |
| H | 11.55527661419572 | 1.92825837824322 | 11.01741284513015 |
| C | 13.38614801593206 | 3.42157270174504 | 16.86837579505653 |
| C | 14.52194431529232 | 3.51167323664575 | 13.58658971479203 |
| C | 12.13065783462469 | 3.80634938922827 | 13.86098666630004 |
| C | 13.64763656535350 | 5.75305561541530 | 16.05502906012229 |
| C | 13.55349872470714 | 6.82389943036494 | 14.97186017554225 |
| H | 13.51752127285899 | 6.32148526235846 | 13.99101818953252 |
| C | 11.86599045807072 | 4.64505258781200 | 11.59100702124420 |
| H | 10.84905044889735 | 4.93813570540642 | 11.91666609558757 |
| H | 12.51947815954683 | 5.49532646467461 | 11.86818070259503 |
| C | 11.58413013101014 | 1.71945791186477 | 17.25385429073390 |
| H | 11.58377442232744 | 1.82495989169941 | 18.35327423334261 |
| H | 11.22736595942942 | 0.70358012932101 | 17.00826726366876 |
| H | 10.84409930383446 | 2.43991801066718 | 16.86610752641285 |
| C | 13.84023617792084 | 3.11743643546305 | 12.25396881063040 |
| H | 14.02712857978440 | 2.05387569281067 | 12.03075100933509 |
| H | 14.26542122002142 | 3.69525305019170 | 11.41589282619633 |
| C | 13.57671706650128 | 3.89274883767434 | 18.18143280944548 |
| H | 13.51166683148691 | 3.18335885863042 | 19.01496925389052 |
| C | 11.68288848626732 | 0.93112674866482 | 12.93611885658634 |
| H | 10.99029964257307 | 0.11972570337219 | 12.65363695571885 |
| H | 11.52256140874930 | 1.13032161899640 | 14.01057776440010 |
| H | 12.71032742123081 | 0.54333524243283 | 12.81148084055310 |
| C | 9.87344975515480 | 5.24236908616232 | 16.83162054101293 |
| H | 10.84715813552647 | 5.07990014061309 | 17.34248443558627 |
| H | 9.84518722467085 | 6.32189265348261 | 16.55803239302481 |
| C | 14.75786973874409 | 7.78141861397027 | 14.96973320357702 |
| H | 14.78511696352523 | 8.39630693079720 | 15.88690858836807 |
| H | 14.68985807925540 | 8.47605538531643 | 14.11372903007288 |
| H | 15.71909242360036 | 7.24400579915091 | 14.90056178816215 |
| C | 13.82864352684080 | 6.16338506669817 | 17.38939763822664 |
| H | 13.96099566176313 | 7.23018093206809 | 17.60447950610916 |

| | | | |
|---|---|---|---|
| C | 13.81307894533136 | 5.24549035498367 | 18.44406362364720 |
| H | 13.95347172488495 | 5.58987602661163 | 19.47545493599548 |
| C | 15.25541393808347 | 2.33759428101920 | 14.24373459899195 |
| H | 15.63657776424371 | 2.60967215734090 | 15.24278182981444 |
| H | 16.11945911392179 | 2.06077508294170 | 13.61541985706233 |
| H | 14.60732280800196 | 1.45151338225921 | 14.33894003944995 |
| C | 8.70740604850961 | 2.18248770990427 | 14.92548137765059 |
| C | 14.00344618020571 | 0.97639698258966 | 17.27961948179302 |
| H | 15.02130704111999 | 1.12735397129332 | 16.88194007377781 |
| H | 13.70066935536871 | -0.06350602022250 | 17.06274121174396 |
| H | 14.05534500069592 | 1.07968660190660 | 18.37824843479663 |
| C | 15.49661773541007 | 4.68379097709656 | 13.42980419708539 |
| H | 15.04334722912690 | 5.53245614251866 | 12.89299482650109 |
| H | 16.36758705102897 | 4.34182356980480 | 12.84469456644332 |
| H | 15.86471848310529 | 5.03482954523214 | 14.40862320434179 |
| C | 11.87829464643198 | 4.46875387238974 | 10.07134105865842 |
| H | 11.63463601233654 | 5.42775342089213 | 9.58198086431596 |
| H | 11.13061984532057 | 3.73007494518280 | 9.73558203421947 |
| H | 12.86650076975057 | 4.14607933124484 | 9.69491006875603 |
| C | 12.23735105664964 | 7.60939587974317 | 15.11194565642908 |
| H | 11.36092538135643 | 6.94730403426045 | 15.01651145647401 |
| H | 12.16317413746867 | 8.38785525510195 | 14.33285549584602 |
| H | 12.16550027373380 | 8.10167226275607 | 16.09819333350705 |
| C | 8.46611560379011 | 6.30071800263042 | 19.44323201217837 |
| H | 9.40707834876794 | 6.26415717053976 | 20.02284396949621 |
| H | 7.62497574345133 | 6.14722604625282 | 20.14504008193083 |
| H | 8.37394538409032 | 7.31691853239003 | 19.01720639330503 |
| C | 8.58270231391865 | 3.28772900929559 | 18.90212083112610 |
| H | 8.53397751584341 | 2.46027991501606 | 18.17175844077370 |
| H | 7.75128320415535 | 3.15748932223981 | 19.61889522699017 |
| H | 9.53034233796511 | 3.18982471699377 | 19.46355234649146 |
| C | 6.80624529804899 | 5.12102883859423 | 17.14540357586498 |
| H | 6.71966574915133 | 6.09609769728229 | 16.63059513277910 |
| H | 5.95553669551664 | 5.03161118044507 | 17.84551560248988 |
| H | 6.69979678092982 | 4.32920081682323 | 16.38226755852450 |
| C | 7.72165925012933 | 1.68540621883363 | 11.98728444940550 |
| H | 6.85596174070990 | 1.36640829022950 | 11.37796196525902 |
| H | 8.56089556556402 | 1.00515007326489 | 11.75159969872696 |
| H | 7.99927432421048 | 2.70631048238695 | 11.66710057493985 |
| C | 7.03214078492050 | 7.86609671686273 | 11.90715477507450 |
| H | 7.00122791436483 | 7.31682178748801 | 10.94802114182002 |
| H | 7.05459322852210 | 8.94866340804478 | 11.68081340896125 |
| H | 6.09114558412570 | 7.64923083187627 | 12.44550161064318 |
| C | 10.08386018120951 | 7.80739486150661 | 11.93127677436942 |

| | | | |
|---|---|---|---|
| C | 8.52345805051023 | 5.49754713617935 | 13.33698122726887 |
| C | 6.75135341372665 | -0.16733807249958 | 14.21269107024778 |
| H | 6.43770595908236 | -0.27241726721722 | 15.26762547905092 |
| H | 7.59344070852919 | -0.86426704512693 | 14.04397306028924 |
| H | 5.90896970160201 | -0.48870316199591 | 13.57183783907552 |
| C | 5.74150796316505 | 2.72671551255100 | 14.09835995677373 |
| H | 5.94314755898707 | 3.77745296777626 | 13.82386982302225 |
| H | 5.40760128883647 | 2.70752409160651 | 15.15181722055566 |
| H | 4.90378687412665 | 2.36673275883738 | 13.47319982837596 |
| H | 9.48410734065222 | 1.38648944902580 | 14.87127573939030 |
| H | 8.34351163781370 | 2.16309761726376 | 15.97814778044533 |
| H | 11.01827157640878 | 7.54589415479160 | 12.45747192554637 |
| H | 10.09611498913710 | 8.89439963665112 | 11.72967966060915 |
| C | 8.49512050234047 | 8.36401147405927 | 14.54462025515762 |
| H | 7.60231031256865 | 8.10156443501900 | 15.14203877006378 |
| H | 8.43945109212422 | 9.44343992173138 | 14.31253736921714 |
| H | 9.38033142155036 | 8.19587410932783 | 15.18210879147091 |
| H | 10.08532792747968 | 7.28691127595908 | 10.95534074921186 |
| H | 7.55894797214698 | 5.30615531711105 | 13.86671505918497 |
| H | 8.43535050755876 | 4.93691119552026 | 12.37858197034041 |

**Table S19.** Cartesian coordinates for the optimized structure of $(^{Me}CAAC)_2YI_3$.

| | | | |
|---|---|---|---|
| I | 8.43900499965960 | 8.92975849661401 | 8.41608690993044 |
| I | 11.53892123540114 | 7.03737149838772 | 11.60487188820066 |
| I | 12.01581624855563 | 12.01482799674736 | 9.33205386228921 |
| Y | 10.86029472711615 | 9.35789173832260 | 9.90736746365177 |
| N | 12.65240835507051 | 7.26431572525180 | 7.65866232168226 |
| N | 9.13350533453257 | 11.44113028427147 | 12.20865455086640 |
| C | 10.21839935483857 | 10.70273392080848 | 12.02522388768550 |
| C | 14.89852637997660 | 7.10362847147472 | 8.37142962570342 |
| H | 15.92674060935010 | 7.24084365156471 | 7.99344229147640 |
| H | 14.94372722031281 | 6.39996599642778 | 9.22303603805162 |
| C | 12.76378094868022 | 8.23064678970382 | 8.55855994273897 |
| C | 10.61901645438835 | 5.86805923128137 | 7.15902524771828 |
| C | 7.87270848620121 | 11.26271404756901 | 11.49751653058695 |
| C | 14.25863026455084 | 8.42634759648393 | 8.84682997519598 |
| C | 11.15882927196189 | 10.95557857930410 | 13.21248114669525 |
| C | 7.44409866712655 | 9.09267283552962 | 12.89248008023063 |
| H | 8.43127428432240 | 9.35360801542008 | 13.30421435442724 |
| C | 14.60003700680850 | 8.74707526011551 | 10.30752340474741 |
| H | 14.26305588688449 | 7.95225334966160 | 10.99266682431680 |
| H | 14.13130119851106 | 9.69887438565114 | 10.61530786281710 |
| H | 15.69364424046742 | 8.87083839408569 | 10.41239752765228 |
| C | 7.03452847870074 | 10.17971194190690 | 11.90126000042804 |
| C | 5.76304458114695 | 10.06539061813075 | 11.30998879607587 |
| H | 5.11505442096709 | 9.23190512327113 | 11.60623895355087 |
| C | 11.45393039997558 | 6.98737345138999 | 6.87450549335366 |
| C | 7.60548832060874 | 7.73512236912549 | 12.18296653799919 |
| H | 6.64082791796215 | 7.38200510884296 | 11.77458594790487 |
| H | 7.98396474668805 | 6.97425676383916 | 12.88860103144516 |
| H | 8.31335042189698 | 7.79399398125000 | 11.34107384116306 |
| C | 7.46147511572926 | 12.16597399255019 | 10.47473274325998 |
| C | 13.96144241136634 | 6.53439838371075 | 7.29324193946916 |
| C | 8.34449424002524 | 13.23796472456222 | 9.83643241859190 |
| H | 9.33026369757691 | 13.22038622487309 | 10.33574531757496 |
| C | 10.71009023466557 | 4.99361098711578 | 8.40926757485937 |
| H | 11.55718366660075 | 5.35050258520436 | 9.02274417594007 |
| C | 9.29410981205073 | 6.40658439997793 | 5.16540234331388 |
| H | 8.45461546561391 | 6.17520385282114 | 4.49866946388455 |
| C | 11.06831870478872 | 10.37416065632011 | 5.72475902314113 |
| H | 10.18082697232251 | 10.38678376638284 | 5.06594672368936 |
| H | 11.64818746591473 | 11.29733978885986 | 5.54617571159110 |
| H | 10.70444924383451 | 10.40354023509208 | 6.76378970002745 |
| C | 14.38561968121468 | 6.85193121276558 | 5.85230214463443 |
| H | 13.61348137656826 | 6.51766047518325 | 5.13842964215304 |

| | | | |
|---|---|---|---|
| H | 15.31582662659829 | 6.30236321060921 | 5.62637525986132 |
| H | 14.57763055138669 | 7.92166907144329 | 5.68467829477351 |
| C | 9.43664767984621 | 5.15161967927860 | 9.26544831254856 |
| H | 9.22324054551254 | 6.20772569317039 | 9.49043320161842 |
| H | 9.55435219725789 | 4.61450472414691 | 10.22295805136725 |
| H | 8.55555088109514 | 4.73694471227438 | 8.74223757228322 |
| C | 5.31996095284646 | 10.97531626276036 | 10.34795050151598 |
| H | 4.32367670158354 | 10.86881034924632 | 9.90196456688356 |
| C | 14.74295808775284 | 9.62696649898461 | 7.98768764979450 |
| H | 15.82189322897989 | 9.77789710092018 | 8.17406643908343 |
| H | 14.20565836314327 | 10.54934358771866 | 8.26395380925682 |
| H | 14.60592577938121 | 9.46448743411105 | 6.90720343111521 |
| C | 11.17455304046740 | 7.84947604598396 | 5.77148515835901 |
| C | 8.58900215374560 | 12.91348016324354 | 8.34818146675515 |
| H | 8.98194374882992 | 11.89463052053912 | 8.20998477259670 |
| H | 9.31912665153530 | 13.62287547211025 | 7.92044628727232 |
| H | 7.65094669227519 | 12.99121295625137 | 7.76844895994417 |
| C | 10.08879614770894 | 7.53137407818770 | 4.93524822418018 |
| H | 9.85943477349081 | 8.19309530706843 | 4.09158017337634 |
| C | 9.55604677956552 | 5.59968142617019 | 6.27400557660838 |
| H | 8.90075893688815 | 4.74585348903960 | 6.48293533036759 |
| C | 6.17211722058095 | 11.99971051067467 | 9.93145959308673 |
| H | 5.84366550548700 | 12.68200134090636 | 9.13856597145260 |
| C | 11.94096877752919 | 9.13299576677862 | 5.46134557771762 |
| H | 12.79760974850869 | 9.20005034604754 | 6.14905101390322 |
| C | 6.45624099250028 | 8.95292868179955 | 14.06620857946115 |
| H | 6.27761447163893 | 9.90938169871821 | 14.58522297992335 |
| H | 6.84403612126473 | 8.22729616769699 | 14.80405141897519 |
| H | 5.47716840627088 | 8.57441317940840 | 13.72057756349100 |
| C | 10.95754486292330 | 9.79631143270692 | 14.22730348986053 |
| H | 9.91994457646260 | 9.71051662162912 | 14.58583371590985 |
| H | 11.60482953549748 | 9.98275981084910 | 15.10363453062760 |
| H | 11.24161458548204 | 8.82993229205281 | 13.77945395290055 |
| C | 12.65124094927955 | 10.99182995940799 | 12.85904711418487 |
| H | 12.97771006333983 | 10.01993967590306 | 12.44755757310038 |
| H | 13.24280523817026 | 11.17625023003194 | 13.77464629073665 |
| H | 12.88004763180214 | 11.77790304689323 | 12.12136739685323 |
| C | 9.17479283556153 | 12.40553671391073 | 13.41177658547719 |
| C | 10.90207362864477 | 3.49673535369932 | 8.09427479096338 |
| H | 10.01225190042600 | 3.08587125944341 | 7.58326178950875 |
| H | 11.02988952740399 | 2.92919695348527 | 9.03368778999906 |
| H | 11.77373950273484 | 3.29364393954375 | 7.45232951642431 |
| C | 12.48351265681506 | 9.16730883961447 | 4.02008181029173 |
| H | 11.66187074123793 | 9.23276183433276 | 3.28395582008317 |

| | | | |
|---|---|---|---|
| H | 13.08016036993250 | 8.27310868888237 | 3.77300704926152 |
| H | 13.12128114825199 | 10.05827113214570 | 3.87587736332855 |
| C | 13.81434807672282 | 5.01928951946990 | 7.42182346526519 |
| H | 13.48440681273477 | 4.72490890162569 | 8.43055355239586 |
| H | 14.79918492878761 | 4.55553019499832 | 7.23517051221627 |
| H | 13.10692206139656 | 4.61971040662365 | 6.67697078182510 |
| C | 10.66103048529075 | 12.29904627975323 | 13.78991440362461 |
| H | 10.81594052620858 | 12.37744249014031 | 14.88021105735879 |
| H | 11.21883249611053 | 13.12425228005077 | 13.30977328012270 |
| C | 8.79782842369631 | 13.82957376230555 | 13.00817861023269 |
| H | 9.44084566722013 | 14.20831460402960 | 12.19844672371518 |
| H | 8.92914034098363 | 14.48735867712880 | 13.88557585060820 |
| H | 7.74293364270985 | 13.89273024476440 | 12.69446166541824 |
| C | 8.20728271096115 | 11.94931170704816 | 14.51297001414058 |
| H | 7.17001211665690 | 11.93878989498807 | 14.13698887518989 |
| H | 8.25668127925222 | 12.66735331062047 | 15.34980539379965 |
| H | 8.44645721027001 | 10.95213445428826 | 14.90977010478489 |
| C | 7.74692565909276 | 14.65578720949108 | 9.93330326717705 |
| H | 6.82117466328124 | 14.73230322640401 | 9.33435198032090 |
| H | 8.46119559257245 | 15.39330187183454 | 9.52483771910310 |
| H | 7.49862723747761 | 14.95594079676111 | 10.96354916489983 |

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